Comments Received on the Draft "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources"

In response to the draft report "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources", which was posted on the EPA website December 31, 1998, comments were received from eight reviewers. They are presented here in alphabetical order by reviewer. Each reviewer's comments have been numbered so that each comment may be addressed individually.

For easier viewing, an outline of reviewers and their numbered comments may be obtained by selecting "View" and then "Bookmarks and page". The outline that appears on the left side of the screen is linked to the document, so that clicking on a reviewer or comment will bring up the appropriate section of the file.

Comments were received from the following groups:

1. Aluminum Association
2. American Forest & Paper Association (AF&PA)
3. American Iron & Steel Institute/American Coke and Coal Chemicals Institute Coke Oven Environmental Task Force (COETF)
4. Council of Great Lakes Industries (CGLI)
5. Halogenated Solvents Industry Alliance (HSIA)
6. Pentachlorophenol Task Force (PTF)
7. Rubber Manufacturers Association (RMA)
8. The Society of the Plastics Industry (SPI) Vinyl Institute

Comments Received from the Aluminum Association

February 25, 1999

Mr. Frank Anscombe
USEPA (G-17J),
77 W. Jackson Blvd.,
Chicago, IL 60604

Dear Mr. Anscombe:

This letter is in response to our review of the aluminum production related sections of the EPA draft report AGreat Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources@ prepared by Battelle Memorial Institute (December 22, 1998). Our comments on the draft report address the discussion of octachlorostyrene emissions formation potential from primary and secondary aluminum processes and follow in the order of appearance in the draft report.

1 Aluminum Degassing (section 4.8)

The draft report outlines OCS formation from the use of hexachloroethane (HCE) fluxing agents in secondary aluminum operations to recover reclaimed aluminum. The report is correct in attributing potential OCS formation with HCE flux usage. The attached table (1) outlines the use of HCE fluxing agents in the US for the secondary aluminum production industry. To address the potential for OCS emissions in the secondary aluminum industry, we have reviewed data gathered during the development process for secondary aluminum Maximum Achievable Control Technology (MACT) standards. EPA gathered data for the secondary aluminum MACT under a Clean Air Act section 114 Information Collection Request (ICR), receiving input for 686 furnaces in the US. The data indicate that the use of HCE as a secondary aluminum fluxing agent is very rare in this country. Of 686 furnaces included in the ICR data base, only 13 small secondary aluminum furnaces report using HCE as a fluxing agent. No large secondary aluminum operations use HCE as a fluxing agent in the US, and none of the reported furnaces were in facilities that are members of the Aluminum Association. As a result, the potential for OCS emissions as a result of HCE flux usage in secondary operations is very low, and is essentially zero in the US for our Association members.

Table 1

Hexachloroethane Usage in the US Secondary Aluminum Production Industry

Location	ICR Furnace #	Furnace Type	Aluminum Production (TPY)	Controls
Gnadenhutten, OH	132	holding	18,000	baghouse with lime
Ft. Wayne, IN	404	melting	125	none
Ft. Wayne, IN	405	melting	125	none
Ft. Wayne, IN	406	melting	125	none
Ft. Wayne, IN	407	melting	125	none
Ft. Wayne, IN	408	melting	125	none
Ft. Wayne, IN	409	melting	125	none
Ft. Wayne, IN	198	melting	947	none
Ft. Wayne, IN	199	melting	125	none
Los Angeles, CA	280	holding	17,100	none
Haytl, MO	140	melting	10,000	none
Bryan, TX	129	reverb	3,500	baghouse
Bryan, TX	130	reverb	3,500	baghouse
Total Production			**53,922**	

Source: USEPA Secondary Aluminum Production Maximum Achievable Control Technology (MACT) Information Collection Request (ICR), 1992/1993.

EPA should also be aware that the data in Table 1 is at least five years old. There has been a generally recognized trend to move away from HCE flux usage in secondary aluminum in the US and abroad. Therefore, the table may represent historical HCE usage levels no longer occurring in the industry.

2 Concerning the formation of OCS from other operations in secondary aluminum, there has been no reported connection that the formation of OCS occurs using other fluxing agents including chlorine without the addition of HCE.

3 A statement at the end of section 4.8 on aluminum degassing is in error. The statement reads:

A[T]he use of argon gas in the degassing of aluminum smelts apparently suffices as a substitute for chlorine or chlorinated degassing agents, without the undesirable generation of chlorinated organic compounds.@

This statement is not factual since many products and charge materials developed and utilized in secondary aluminum cannot be processed satisfactorily without the use of chlorine fluxing agents to remove impurities and/or gas bubbles. The use of argon gas as a chlorine substitute is occurring in the industry where possible. However, chlorine is still a necessary fluxing agent for a number of process/product operations. The statement noted above should be deleted from the report.

4 Secondary Aluminum Smelting (section 4.0)

This section, which is somewhat redundant to the section on aluminum degassing, suggests that OCS is formed from the use of chlorine or sodium chloride and fluoride salts. This assertion is hypothetical, and we believe not a viable possibility in secondary aluminum processing. The fluxing agents used in secondary aluminum processing, besides HCE, do not contain the highly chlorinated alkanes or alkenes necessary to facilitate OCS formation. In secondary processing the charged metal is preconditioned or heated during melting to remove coatings and organics before fluxing. Organic materials present on the charged material is driven off prior to the introduction of fluxing agents. Subsequent use of chlorine, salts and other fluxing agents that do not contain the requisite chlorinated alkanes or alkenes will not promote the formation of OCS. Only HCE fluxing agents have that potential, as discussed above in these comments.

5 Primary Aluminum (section 4.20)

The draft report outlines the potential for OCS formation from the AAlcoa Smelting Process@ which utilizes aluminum chloride in an electrolytic process. This process is not in use in the US at any facility that we are aware of, including all Aluminum Association members. All primary aluminum facilities utilize the following process:

Primary aluminum is produced using the Hall-Heroult electolytic process. In this process, aluminum production is carried out in a semi-batch manner in large electrolytic cells called pots with a dc input of up to 280,000 amperes and about 5 volts. The pot is a rectangular steel shell typically 30 to 50 feet long, and 9 to 12 feet wide, and 3 to 4 feet high, and is lined with a refractory insulating shell on which carbon blocks are placed to form a cathode. Steel collector bars are inserted into the cathode blocks to carry current away from the pot. Molten cryolite (sodium-aluminum fluoride) is placed in the cavity formed by the cathode blocks. Anodes, also of baked carbon, are immersed in the cryolite to complete the electrical path. Anodes may be either pre-baked in a separate process and attached to connecting rods for immersion into the bath (termed Prebake design cells), or may be formed through self-baking from coal-tar

and petroleum coke paste that is fed into the top of a steel casing above the cell (termed Soderberg design cells). Alumina (Al2O3) is fed in powder form into the pots by various design means and is dissolved in the cryolite bath.

The potential for OCS from primary aluminum production using the Hall-Heroult process is essentially zero since there is no source of chlorine.

The section on Primary Aluminum in the report further describes an additional process to purify aluminum subsequent to production, through a three layered electrolytic process. This process is not in operation in the US to our knowledge based on information available from our membership. Therefore, the potential for OCS formation from the purification process outllined in the draft report is likely to be zero in the US.

Potential Sources of OCS (section 4.3, Table 2)

6 Table 2 in the draft report that outlines potential sources of OCS needs to be revised to reflect the comments included in this submission. Specifically, the Adocumented@ section of sources includes a secondary aluminum smelting reference that reads: AVaporization of chlorinated organic coatings in used beverage containers; use of chlorine in demagging.@ This statement should be revised read: **ARemoval of contaminants with the addition of hexachloroethane fluxing agents.@** There are no other documented OCS sources in secondary aluminum. Similarly, the section in Table 2 on Primary Aluminum that refers to AElectrolytic purification or manufacture of aluminum using a chloride salt and graphite electrodes@ should be removed. The electrolytic purification process noted in the table is not in use in the US to our knowledge and is therefore not a possible source for OCS.

Potential National OCS Emissions by Source Category (Section 4.24, Table 4)

7 Included in Table 4 is an estimate of OCS emissions from secondary aluminum smelting totaling over 11,000 grams per year. This estimate needs to be revised significantly to reflect the much smaller use of HCE fluxing agents outlined in this submission.

We hope that this information is useful in your efforts to revise the draft OCE report. Please contact my office (202/862-5132) if I can be of further assistance.

Sincerely yours,

Robert P. Strieter
Director, Environmental Affairs

xc: J. Green
S. Larkin
Baker & Hostetler
G. H. Cooper

A F & P A
AMERICAN FOREST & PAPER ASSOCIATION
Regulatory Affairs

March 1, 1999

(Via Fax)

Elizabeth LaPlante
U.S. EPA, Great Lakes National Program Office
77 West Jackson Boulevard
G-17J
Chicago, Illinois, 60604.

Re: AF&PA Comments on Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources (Report) 63 *Federal Register* 72,311 (December 31, 1998)

Dear Ms. LaPlante:

AF&PA appreciates this opportunity to provide comments on the A Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources (Report) AF&PA participated extensively, both on its own, and as a member of the Council of Great Lakes Industries (CGLI), in the early development of the Great Lakes Binational Strategy (BNS). AF&PA supports CGLI=s comments filed today on several BNS issues. Also, forest products industry representatives have actively participated in several of the substance-specific Workgroups, including the OCS Workgroup.

1 As an initial matter, we must express our disappointment with the manner in which the Report was developed. The OCS Workgroup had been making significant progress on identifying potential sources of OCS and developing a potential action plan. The release of the Report to the public before providing an opportunity for Workgroup review has significantly hampered that progress, and diverted Workgroup members= attention from that progress. We strongly suggest that future reports be provided to Workgroup members for initial review before distribution to the public. Had that review occurred with the Report, many of its inaccuracies and incorrect assumptions could have been resolved before wider, public distribution.

2 In comments submitted under separate cover by the Council of Great Lakes Industries (CGLI), information is provided which is highly suggestive that the levels of OCS in the ambient environment are continuing to decrease. These trends do not support the existence of significant (if any) ongoing or unidentified sources of OCS. Given that the data do not support evidence of significant ongoing sources, speculation about potential new sources is not warranted and does

not serve the purposes of the Binational Toxics Strategy. A more critical examination would be far more appropriate to assure that resources are directed only where needed. We suggest that EPA subject the Report to a thorough peer review process to determine whether some of its underlying assumptions withstand such a critical scientific review. Such a review would help ensure that both public and private resources are directed only where needed.

3 In the attached comments, which is confined to a review of some of the chemistry information supporting the identification of potential OCS sources in the Report, NCASI has conducted a critical examination of the most probable reaction mechanism and reaction conditions for known sources of octachlorostyrene vs. other potential sources. That examination clearly indicates there is no technically defensible justification for hypothesizing OCS formation in several manufacturing processes discussed in the Report, including the processes associated with the forest products industry. Finally, there are fundamental flaws in the underlying technical assumption used in the proposed approach to use known sources or inventories of hexachlorobenzene or PCDD/F to predict or develop an OCS inventory.

Again, thank you for this opportunity to com ment on the Report. We request that the final version of the Report reflect the information we are providing today. If you have any questions about this material, please feel free to call me at (202) 463-2581. If your questions are of a technical nature, please contact Larry LaFleur, NCASI, at (541) 752-8801. Thank you for your attention to this matter.

Sincerely,

Jerry Schwartz
Director
Water Quality Programs

Attachment

cc: Frank Anscombe, EPA

American Coke and Coal Chemicals Institute

1255 Twenty-Third Street, NW • Washington, DC 20037-1174 • (202) 452-1140 • Fax: (202) 833-3636

March 22, 1999

Mr. Frank Anscombe
U.S. Environmental Protection Agency
Region 5 (G-17J)
77 West Jackson Boulevard
Chicago, IL 60604

Mr. Darryl Hogg
Canada Ontario Agreement Coordination
Ministry of Environment
40 St. Clair Avenue West, 12th Floor
Toronto, Ontario M4V 1M2

Re: BMI's December 12, 1998, Draft Report Implicating Coke Production as a Possible "Suspect Source" of OCS Emissions

Gentlemen:

I am writing on behalf of the AISI/ACCCI Coke Oven Environmental Task Force (COETF), concerning a 12 December 1998 draft report entitled "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources". The draft report was prepared by Batelle Memorial Institute (BMI) for the EPA.

1 The COETF (see Enclosure 1) was formed in 1996 by the American Iron and Steel Institute (AISI) and the American Coke and Coal Chemicals Institute (ACCCI) to address environmental issues of concern to the industry. The COETF represents all 20 U.S. companies that produce metallurgical coke, including nine integrated steel companies operating 14 coke plants (40 batteries) and 11 independently owned/operated "merchant" companies operating 11 coke plants (28 batteries). The COETF also represents two Canadian companies that produce coke.

The COETF is vitally interested in the draft report because it implicates coke production as a possible "suspect source" of OCS emissions. Upon first learning of the draft report via its involvement in the Council of Great Lakes Industries (CGLI), the COETF provided CGLI with the results of effluent testing at Stelco Inc.'s Lake Erie Steel Company. These results, which showed no detectable OCS in coke plant effluent (see Enclosure 2), were provided to CGLI for submittal to Great Lakes Binational Toxics Strategy (BNTS) OCS Workgroup. CGLI submitted this information to the Workgroup on March 1 (see Enclosure 3).

2 Subsequently, the COETF retained Dr. Laura L. Kinner (Emission Monitoring Inc.), to evaluate the potential for OCS formation in coke ovens. Dr. Kinner, an expert in coal chemistry, has concluded that " ... the formation of OCS during coal coking operations is not implicated by the reaction mechanisms, nor do laboratory studies or actual emissions data support it" (see Enclosure 3). A copy of Dr. Kinner's resume is enclosed for your information (see Enclosure 4)

In consideration of the above, we believe the evidence is compelling that coke plants are not a source of OCS and hereby request that coke production be removed as a suspected source of OCS emissions. Please call me if you have any questions.

Sincerely,

David C. Ailor, P.E.
Director of Regulatory Affairs

Four Enclosures

cc (w/o Attachment to Enclosure 3):
COETF (see Enclosure 1)
Jeff Wentz (Acme Steel Company)
Bob Ajax (Ajax & Associates)
Marty Dusel (Citizens Gas & Coke Utility)
George Kuper (CGLI)
Ian Shaw (Dofasco, Inc.)
Gary Quantock (DTE Energy Services)
Laura Kinner (Emission Monitoring Inc.)
Steve Sands (Geneva Steel)
Gerald Kendrick (Jewell Coal & Coke)
Traci Self (Koppers Industries, Inc.)
Mary Lou Harmon (LTV Steel Company)
David Menotti (Shaw, Pittman, Potts & Trowbridge)
Bob Bloom (Tonawanda Coke Corporation)
Nancy Hirko (USS)

R024h

ENCLOSURE 1

AISI/ACCCI Coke Oven Environmental Task Force

Bill West, Co Chairman	LTV Steel Company
Ron McCollum, Co Chairman	USS Clairton
Mark Poling	ABC Coke
Jack Garzella	Acme Steel Company
Steve Felton	AK Steel Corporation
George Ossman	Bethlehem Steel Corporation
Wade KohImann	Citizens Gas & Coke Utility
Danny Lewis	Empire Coke Company
Russ Christensen	Geneva Steel
Buster Stewart	Gulf States Steel, Inc.
George Bradley	Indiana Harbor Coke Company
Greg Shamitko	Koppers Industries, Inc.
Jack Heintz	National Steel Corporation
Mike Mehalovich	New Boston Coke Corporation
Nick Buchko	Shenango Inc.
Bobby Fisher	Sloss Industries Corporation
Tim Huxley	Stelco Inc.
Mark Kamholz	Tonawanda Coke Corporation
Bill Samples	Wheeling-Pittsburgh Steel Corporation

ENCLOSURE 2

Stelco Inc.
General Office
Stelco Tower
Hamilton, Ontario
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(905) 528-2511 ext 4201
fax (905) 577-4441
e-mail environ2@stelco.ca

1999-02-10

Mr. David C. Ailor, PE
Director of Regulatory Affairs
American Coke and Coal Chemicals Institute
1255 Twenty-Third Street, NW
Washington, DC 20037

Dear Mr. Ailor: Dave

Subject: **OCS in Effluent - Test Results from Stelco**

The Ontario government tested integrated steel plant effluents in 1989 and 1990 for various pollutants including OCS, as part of its Municipal/Industrial Strategy for Abatement (MISA).

OCS was below detection at all facilities including Stelco Inc.'s Lake Eric Steel Company, which produces over 600,000 tons of coke annually, but due to an unfortunate error made in recording the data the government earmarked Lake Erie Steel Company as an OCS emitter.

Lake Erie Steel Company effluent measured less than 0.0026 ug/l OCS i.e., below detection limit, for all samples taken between November 1989 and June 1990, the government test period. The RMDL was 0.010 ug/1.

Enclosed are copies of correspondence between Stelco and Mr. Daryl Hogg, a consultant working for the Ontario Ministry of Environment and Environment Canada on Great Lakes issues including the Binational Agreement.

The result of that dialogue was the conclusion by government that the Iron and Steel Sector is not a source of OCS, and they now reflect this in their OCS survey.

Best regards,

FRK

F.R. Kent
Environmental Program Specialist

cc T.F. Huxley

Canada Ontario

June 11, 1998

FRK 06/15 COP Jan

c.c. G. Saldanha
T. Huxley

orig to file with "COA"

12 Floor
40 St. Clair Avenue West
Toronto, Ontario
M4V 1M2
Tel.(416)-314-3931

Mr. Ross Kent
Environmental Program Specialist
Stelco Inc.
General Office
100 King St. West
Hamilton, Ontario
L8N 3TI

Dear Mr. Kent:

Thank your for your letter of May 26, 1998, concerning the Octachlorostyrene release number for the Lake Erie Steel Company Ltd. (LESC).

Your letter and the MISA records from LESC indicating that OCS levels were below detection limits over the MISA sampling period in question are presently under review. Once I have received concurrence on your findings, I will inform you. In the interim period, the OCS number attributed to the iron & steel sector in the COA inventory of tier I/II substances has been removed, and replaced with a notation that the release number is under review.

If you have any questions on the above matter please contact me.

Yours truly,

Hogg

Darryl Hogg
COA Stream 2 Coordination

cc. Ian Smith
Tom Tseng

NOTE TO FILE 02/10/99

- D. Hogg confirms that IRON and Steel Sector is NOT a suspect for OCS.
He concurs that an error was made in MOE 1990 REPORT.
- He is involved in BINATIONAL AGREEMENT ON GL talks.

per Telecon D. Hogg / FRK. FRK.

May 26,1998

Our Ref: COA

Mr. Darryl Hogg
Canada Ontario Agreement Stream 2 Coordination
Program Development Branch
Ministry of Environment
40 St. Clair Avenue West 12 Floor
Toronto, Ontario
M4V 1M2

Dear Mr. Hogg: **OCS Release from Lake Erie Steel Company Ltd. (LESC)**

Thank you for the opportunity to review the COA background information on how the octachlorostyrene (OCS) re[ease to water for Iron and Steel was derived.

LESC environmental staff, having reviewed the MOE report on OCS that you faxed to me on May 14, 1998 and its own MISA records from the time period, has concluded that the MOE has made an error. MISA sampling in 1989 and 1990 at LESC found no OCS.

The LESC staff discovered the following:

1. The level of OCS in Pond 4 effluent during the stated time period was always below the detection limit. The MISA reports for November/89 to June/90 are enclosed as evidence.
2. The November/89 number for OCS reveals the turmoil gone through at the beginning of MISA: confusion over reporting in mg/l or ug/l, and confusion over using RMDL or LMDL. Note that the current version of MIDES automatically inserts the RMDL figure when none detected" (F3) is keyed.
3. It would appear that the MOE dropped the <" (less than) sign from the LESC report.

In light of the above, subsequent to your review and concurrence with our findings, please revise the OCS inventory in the COA substance profile to remove LESC as a source.

We would be pleased to discuss this further via telephone or in person: we wait for your response.

Yours very truly,
STELCO INC.

FRK

F. R. Kent
Environmental Program Specialist

:frk Att. C:\ross\OCS Releases.doc

Copy (letter only) to: T. Huxley, Stelco Inc.
G. Richardson, CSPA
G. Saldanha, Lake Erie Steel Company Ltd.
T. Tseng, Environment Canada

Potential of Octachlorostyrene Formation from Coke Ovens

Laura L. Kinner Ph.D.'
Emission Monitoring Incorporated
8901 Glenwood Ave.
Raleigh, NC

Introduction

A draft report entitled "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources" was prepared by Battelle Memorial Institute (12/22/98) for the U.S. EPA. The Battelle Report discusses the toxicity and environmental persistent nature of OCS, and presents a detailed list of sources known and suspected to emit OCS. All of the "documented sources" of OCS emissions identified in Table 2 of the report have chlorine as a reactant or by-product of the process. All of the "highly probably" sources of OCS emissions are identified as incinerative in nature and/or have chlorine as a reactant or by-product of the process. Coke production is identified as a possible suspect source" of OCS emissions.

This paper addresses the potential of OCS formation from coke ovens.

Coke Formation by Coal Pyrolysis

Coke formation is not like the other processes identified in the Battelle Report as emitting OCS. The coking process is not incinerative and does not involve the addition of chlorine. Coke is formed by thermally treating coal in the absence of excess oxygen (pyrolysis).

' Dr. Kinner received her Ph.D. from the University of Missouri in 1992. Her dissertation research focussed on gasification of hazardous wastes using coal chars. This work entailed detailed studies of various coals and the reaction mechanisms of pyrolysis, gasification and combustion relative to the destruction highly chlorinated hazardous and radioactive mixed wastes.

Coal is highly amorphous and varies significantly by geographical location and age. Coal can be represented as aromatic and hydroaromatic sub-units with functional groups at their periphery forming a cross-linked structure. The functional groups are mainly hydrocarbon (methylenic or ethylenic) in nature, but can also be composed of sulfur, nitrogen, metals and halogen atoms. Elements such as chlorine generally comprise less than 0.5% of the coal structure. X-ray analysis of coals shows that the cyclic sub-units arrange themselves in polymeric layers becoming more ordered (graphitic) depending on coal rank.[2] In general coal is ranked by hardness; anthracite > bituminous > sub-bituminous > lignite.

When coal is subjected to the pyrolytic conditions encountered during the coking process, the weakest bonds in the cross-linking structure rupture. This thermal decomposition, or cracking, causes two free radicals to be formed for every bond broken. Coal pyrolysis end products are: coke (devolatilized coal) and gaseous mixtures of H_2, CO, $C0_2$, CH_4 (methane), water and lighter hydrocarbons. These products differ greatly from those of combustion: noncombustible residue (ash), CO_2 and H_2O.[3]

An important reactive intermediate of coal pyrolysis is atomic hydrogen [H•], sometimes referred to as nascent hydrogen. The amount of available nascent hydrogen formed during combustion is negligible compared to that formed during pyrolysis.

Potential of Octachlorostyrene Production during Coal Coking

The atomic hydrogen produced during coal pyrolysis reacts with other hydrogen atoms to produce H_2, and participates in reactions with other gaseous free radicals and the hot coal surface. Formation of octachlorostyrene in coal pyrolysis systems is not favored because: 1) chlorine free radicals cleaved from the coal surface during thermal cracking will combine with the nascent hydrogen to form hydrochloric acid (HCl), 2) nascent hydrogen abstracts chlorine from the hot coal surface (dehydrochlorination) forming HCl, and 3) alkychloride free radicals (RCl•) cleaved from the coal surface during thermal cracking will combine with nascent hydrogen or other alkyl free radicals to produce low molecular weight organochloride compounds such as chloromethane, chloroethane, etc.

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2. Cartz, L. and Hirsch, P.B., "A Contribution to the Structure of Coals from X-Ray Diffraction Studies," Proceedings from the Royal Society of London, 1960, A252, 557-602.

3. Campbell, J.H., "Kinetics Studies of Gas Evolution During Pyrolysis of Subbituinous Coal," American Chemical Society, Division of Fuel Chemistry, 1991, 21, 7, 94.

The immediate consumption of chlorine and alkyl chloride free radicals by nascent hydrogen eliminates a multi-step chlorination reaction involving styrene to produce the fully chlorinated compound OCS.

Supporting Data

Pyrolysis and gasification studies were conducted using coal char as a substrate for hexachlorobenzene (HCB) to determine the potential of coal char pyrolysis to dehydrochlorinate hazardous wastes.[4] In these studies, mass balances achieved for chlorine determined that HCB sorbed onto coal char was effectively dechlorinated to HCl and chlorides as determined by analysis of effluent gas and the pyrolyzed chars. No highly chlorinated organic compounds were detected in these studies.

The fact that OCS formation during coking operations is not probable is further supported by information contained in the Battelle Report (cited above) and from data gathered by Bethlehem Steel Corporation (see Attachment). The Battelle report states that:

> "*In general, it appears that whenever hexachlorobenzene (HCB) and chlorinated dibenzodioxins (CDDs) are formed, there is potential that OCS is formed*"

Therefore, the absence of HCB and CDDs would indicate that formation of OCS is not favored.

In the Bethlehem study, untreated effluent samples collected from a coke oven battery using XAD resin were analyzed for semi-volatile compounds by SW846-8270. The results from these analyses indicate no emissions of HCB, or any other chlorinated organic compound from the testing conducted at Bethlehem at stack concentrations of approximately 7.5 parts per trillion (using the level of detection reported by Great Lakes Analytical). Method 18 samples were analyzed for volatile compounds using SW846-8240 analysis procedures during this same testing program. Results from these analyses indicated that one run had methylene chloride contamination as indicated by the field blank. No other organochlorine compounds were detected in any sample at stack concentrations approximating 0.1 parts per billion (using the level of detection reported by Air Toxics LTD). Given these data, it seems highly improbable that OCS is emitted from coal coking operations.

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[4] Kinner, L.L., Manahan, S.E., "Mechanistic Study of the ChemChar Process Using Hexachlorobenzene as a Surrogate for Monitoring reaction Products," Chemosphere, 24 (12) 1867-1884. (1992).

Table 4. of the Battelle Report also contains a list of source categories and their potential to emit OCS. In this Table, carbon reactivation furnaces are listed as having negligible dioxin emissions and negligible potential to emit OCS. It is unlikely that coke production would have a greater potential of OCS emissions relative to carbon reactivation furnaces.

Conclusions

The formation of octachlorostyrene during coal coking operations is not implicated by the reaction mechanisms, nor do laboratory studies or actual emissions data support it. Therefore, coke production should be removed as a suspected source of OCS emissions from Table 2 of the Battelle Report.

March 2, 1999

Mr. Frank Anscombe
U.S. Environmental Protection Agency
Region 5 (G-17J)
77 West Jackson Boulevard
Chicago, IL 60604

Mr. Darryl Hogg
Canada Ontario Agreement Coordination
Ministry of Environment
40 St. Clair Avenue West, 12th Floor
Tontro, Ontario M4V 1M2

Dear Darryl and Frank:

The Council of Great Lakes Industries has reviewed the draft report "Great Lakes Binational Toxics Strategy Octachlorostyrene Report: A Review of Potential Sources. We have contacted knowledgeable individuals within most of the industrial sectors discussed in the report. We and the experts whom we have consulted have found the report to be very seriously flawed. This letter, and an extensive report to the OCS Workgroup which, as planned, will follow within the next several days, detail these findings.

Report Approach

The most serious error regarding this second Battelle OCS report (it follows the initial draft OCS Action Plan) is its approach to the assessment of the status of Binational Toxics Strategy (BNTS) challenges regarding OCS. Rather than take an objective view of whether or not the challenges have been met, the report authors seem to go out of their way to deliberately seek the most minuscule, insignificant, and theoretical potential sources. Certainly CGLI expects a rigorous review of source status. But, we expect this review to be conducted on the basis of confirmation of releases through the use of sound analytical techniques. When measurements fail to link a "suspected" source with actual releases, we do not believe it serves any purpose to continue to suggest a "potential" release based on posed theoretical circumstances. Unfortunately, the report does this in several places.

A second serious oversight is the failure to investigate and acknowledge the absence of certain industry sectors within the Great Lakes Basin. The continued use of a particular

technology at a location far removed from the Basin is not, unless special circumstances prevail, likely to have a significant impact on Basin waters. CGLI's sector review work has shown that several suggested sources or processes do not operate within the Basin. We note that a newly released draft Ontario OCS inventory report, although it may suffer from some of the technical short comings as the Battelle report, does in fact look first to see if the suggested sources are active in Ontario.

As described below, the most serious technical error is the one-size-fits-all approach taken to apply surrogate measurements and calculate potential OCS releases. As explained in the extensive review produced by Mr. Larry LaFleur of NCASI, comments from whom have also been forwarded by the American Forest and Paper Association, the HCB/OCS or dioxin/ocs relationship for a given source is dependent on many variables and must be carefully determined on a case by case basis. In addition, factors like partition coefficients and other important variables must be considered when extrapolations from sediments are made to predict source releases. Mr. Robert Bailey, a member of the HCB Workgroup, has provided the analysis which appears below.

Sector Analysis

CGLI has undertaken a comprehensive review of the OCS sources in the Battelle report on a sector by sector basis. We have contacted industry experts and solicited comments on the basis for which OCS releases have been suggested within the report. This detailed response is in final preparation stages and will be forwarded to the BNTS OCS Workgroup when completed.

Detailed Technical Comments

As mentioned above, Dr. Larry LaFleur of the National Council of the Paper Industry for Air and Stream Improvement has studied the mechanics of chlorinated phenolic compounds extensively. He has reviewed the second Battelle report and has concluded that from a mechanistic and sound scientific process standpoint, the document is seriously flawed. His observations include the following.

Introduction

A fundamental premise of modern synthetic chemistry is that one needs to understand the basic reaction mechanism before one can reliably predict products. Even if one knows the proper mechanism, the appropriate reaction conditions (e.g., temperature, catalyst, sufficient time, proper solvents, suitable concentrations, etc.) must be present in order for the reaction to proceed. Many reactions which occur in one solvent, such as free radical chlorination in aprotic solvents, would be suppressed in a protic solvent such as water. Finally, the necessary starting materials must not only be present, but must be present in proportions conducive to the reaction. In many respects, synthetic chemistry is the science of successfully optimizing the various combinations of these variables to achieve a specific, desired outcome.

Accordingly, any technically creditable extrapolation from known sources of octachlorostyrene (OCS) to potential other sources requires a careful consideration of reaction mechanisms, conditions, and stoichiometry. Thus, sufficient evidence that each of these criteria have been met must be demonstrated before one would have sufficient cause to further examine a hypothesized new source.

Below, we discuss mechanistic considerations, reaction conditions, and stoichiometry of some known sources of OCS. In this discussion, we highlight the types of corroborating data that would be necessary to extrapolate known OCS sources to other sources. We also give several examples of how a more critical consideration of these fundamental principles would show that there are no data to support the hypothesis that these processes are potential sources of OCS. We briefly discuss the Battelle approach to estimating an OCS inventory based on the EPA dioxin inventory and show that the underlying assumptions are fundamentally flawed.

Mechanistic Considerations

Hexachlorobenzene, octachlorostyrene, and PCDD/F

The Battelle report notes an apparent relationship between hexachlorobenzene and octachlorostyrene where PCDD/F have also been reported. These different mechanisms seem to arise where the starting materials and/or conditions are such that hexachlorobenzene can be formed. Apparently, under these same conditions hexachlorobenzene can further react to form octachlorostyrene or it can proceed through a different series of reactions to form PCDD/F. Under these circumstances, there is an apparent relationship between octachlorostyrene and PCDD/F. However, it would be inappropriate to conclude that the reverse would also be true. If PCDD/F are formed by some other mechanism under other conditions, it may or may not coincidentally produce either hexachlorobenzene or octachlorostyrene. As is discussed in Section V, there are several examples of PCDD/F formation where there is no reason to suspect formation of octachlorostyrene.

The de novo synthesis hypothesis

In the review of sources commissioned by EPA in 1985, Schulman and Klingele[1] discussed theoretical mechanisms for octachlorostyrene formation. They proposed the following hypothesis:

> "Each reaction in the stepwise formation of PCSs could fall into one of two broad categories:
>
> 1. ultratrace concentrations of reactants combine in high yield; or
>
> 2. high concentrations of reactants combine in ultratrace yields

[1] For complete description of references see bibliography contained in Appendix I.

In the former case, the free energy of formation of the product at each step is lower than the free energies of reactants and other competing products. In the latter case, the free energies of formation of reactants and other products are lower than the PCS precursor products, but the statistics of the reaction chemistry assure that some of each of the successive precursor products will be generated in some amounts.

Reaction conditions favoring the former case would probably involve high energy environments where polychlorinated aromatics like PCSs would be stable relative to other molecular configurations. Such conditions would be likely to prevail in high energy electro-, pyro-, photo- and thermochemical reaction environments. Reaction conditions favoring the latter case would involve lower energy reactions in which polychlorinated organic substances are reactants or intended products. Further, if PCSs were removed from the reaction environment fastest than other, more stable products, say via physical processes such as sorption to the walls or bottom of a reactor vessel or to particulate matter in the reaction matrix, significant quantities of PCSs could still be generated, even though not thermochemically favored."

Schulman and Klingele (1985) went on to propose a theoretical mechanism that might lead to the formation of octachlorostyrene through a series of high energy free radical chlorinations and polychloro alkyene radical coupling reactions. This mechanism is termed the *de novo* synthesis mechanism. This mechanism was not proposed based on any experimental investigations on their part, but was instead based on their review of potentially relevant published literature and their interpretations.

Their final conclusions based on their deliberations were:

"Whenever a carbon source is exposed to chlorine and large energy flux, as either electricity or heat, and indicator compounds such as carbon tetrachloride, perchloroethylene, and perchlorobenzene are produced, PCS is a suspected byproduct. Whenever aromatic compounds, particularly chlorinated ones, are exposed to conditions where chloroalkyl radicals may be present, PCS is a suspected byproduct."

We would add to those observations the fact that the chemistries used to support their hypothesis were free radical reactions occurring under extremely high energy conditions, and were often conducted with a very large excess of chlorine (relative to the available carbon). We believe these are important distinctions.

The Battelle report cites this hypothesis, describes it generally, but does nothing to further advance it or support it with new information.

Based on the rationalizations used to advance this hypothesis, the *de novo* mechanism is clearly a high energy free radical chlorination and coupling mechanism. In order to invoke this mechanism for a potential new source of OCS, one should provide supporting data to

justify the hypothesis. As discussed in the Schulman and Klingele report, one should provide evidence of other intermediates or by-products that support that a similar mechanism is operative. These may include carbon tetrachloride, various tri- and tetra-choro ethanes and ethylenes, hexachlorobutadiene, di-, tri-, tetra-, penta-, and hexachloro-benzenes, etc. Since many of these are actual commercial products, it would be necessary that more than just a single intermediate be identified to support the like mechanism argument.

Magnesium and nickel refining

In one reference, the Battelle report states that there are indications of formation of both OCS and PCDD/F (Oheme et al. 1989) in magnesium and nickel refining. The authors also note that the processes result in the formation of hexachlorobenzene. Oheme et al. describe a unique PCDD/F fingerprint where the PCDF to PCDD ratio is 50:1. This would indicate that it is appropriate to suggest formation of OCS from a source if, and only if, the hexachlorobenzene was demonstrated to be present and the PCDF to PCDD ration was approximately 50:1. A more detailed examination of the PCDD/F fingerprint reported by Oheme et al. (1989) should be performed, and additional criteria should be considered (e.g., the 1,2,3,7,8-PeCDD to 2,3,7,8-TCDD ratio was 11:1). These criteria would provide a technical justification for assuming a like mechanism might be operative. At the same time, it should also be pointed out that the Oheme et al. work explicitly pointed out the vast differences between the Mg and Ni refining PCDD/F fingerprint and the fingerprint typically observed in incineration sources. This is explicit evidence that there is a completely different mechanism than the one responsible for the OCS from Mg and Ni refining that may be operative in incineration sources.

Other metal refining processes

Doring et al. (1992) describe the concurrent formation of OCS, HCB, pentachlorobenzene (PeCB), decachlorobiphenyl (DCB), and PCDD/F from a copper smelting process. Doring et al. (1992) describe conditions necessary for the formation of these compounds as follows:

> "A chlorine source is present (sodium chloride) and the reductive conditions transform Cl^- to Cl·-radicals. These are then able to chlorinate the aromatics formed by radical processes from the carbon source (coal) at the high process temperature."

They later note:

> "The chlorination roasting process of the copper slag has some similarities with the production of waterfree magnesium chloride (reductive conditions at high temperature (>700°C), presence of carbon and Cl-radicals)."

Much like the fingerprint for the above described Mg process, there is a clear predominance of PCDFs, with the PCDF/PCDD ratio at about 10:1.

This illustrates the importance of corroborating mechanistic hypotheses with confirmatory data. Only when clearly analogous conditions are observed and similar fingerprints are demonstrated (e.g., PCDF/PCDD ratio of 10:1, presence of HCB, DCB, and PeCB) can one reasonably infer the formation of OCS.

Perchloro solvent manufacturing

In the work reported by Pereira et al. (1988), which the Battelle report cites as evidence of a link between OCS and HCB, the authors also report the presence of high levels of di-, tri-, tetra-, and penta-chlorobenzenes, as well as hexachloro-1,3-butadiene and octachloronaphthalene as by-products of chlorinated solvent manufacturing. Thus, before invoking an argument that the presence of HCB is an indication of potential OCS via the same mechanism, evidence of these other co-contaminants that would support the hypothesis of a like formation mechanism should be provided. Otherwise, there is no justification for supposing a like mechanism.

To summarize, before any surrogate chemicals like PCDD/F or HCB can be used as indications of the potential for OCS formation, there should be some corroborative data which provides supporting evidence that a like reaction mechanism is operative. Without such evidence, the extrapolation from one source to others using the presence of these proposed indicator compounds is technically insupportable.

Chlor-alkali production

The Battelle report sites the work of Kaminsky and Hites (1984) as evidence of the formation of OCS in the chlor-alkali process where carbon electrodes are utilized. In work published by Rappe et al. (1990), a PCDD/F fingerprint for this type of process was shown to produce a large predominance of PCDFs. For instance, sludge from electrodes was found to contain 52,000 pg/g 2,3,7,8-TCDF vs. non-detectable levels of 2,3,7,8-TCDD. Similar high ratios were found for the higher homologues. Thus, inferring a relationship between known sources of PCDD/F from electrolytic processes and the potential for production of OCS would only be technically defensible if it were demonstrated that the PCDFs clearly dominated the fingerprint. If another fingerprint is observed, it would be sufficient evidence that an alternative mechanism is operative and that, in the absence of other evidence concerning that mechanism and its by-products, it would be inappropriate to infer the formation of OCS.

Reaction Conditions

Table 1 provides a partial summary of conditions where OCS has been demonstrated to form (as described in the Battelle report, not independently verified). All can be characterized as high energy processes. Some involve high electrical currents, some high temperatures, and some both. In many cases, Cl_2 gas or other chlorinated solvents are used to create certain atmospheres, and conditions are such that they are clearly intended to react. Characterization of other potential sources of OCS should include careful comparison of the conditions known to produce OCS and those of the candidate process.

Table 1. Reaction Conditions of Known Sources of Octachlorostyrene

Process	Temperature	Energy Input	Carbon Source	Chlorine Source
Chlor-alkali	not specified	electric current	carbon electrodes	brine and Cl_2 produced
Mg refining	1000-1200°C	electrodes	carbon electrodes	Cl_2 atmosphere
Al degassing	600°C	unspecified, (sufficient to melt Al metal)	hexachloro-ethane	hexachloro-ethane or Cl_2
Cu smelting	700°C	unspecified, (sufficient to melt Cu metal)	coal	8% NaCl under reducing conditions
Secondary Pb smelting	1260°C	incineration	battery casings	PVC separators

Stoichiometry

Examination of the metals refining processes described in the Battelle report strongly indicates that in most cases there is excess chlorine relative to carbon (high chlorine to carbon ratio). This is also true for the production of carbon tetrachloride and tetrachloroethane. If one considers the chlor-alkali process, where a large volume of Cl_2 is produced from a comparatively small mass of carbon (in the form of the electrodes), there is also a high Cl/C ratio. Under these circumstances, it seems apparent that the potential for the formation of highly chlorinated compounds like OCS exists. However, it would

not be appropriate to assume that if the right temperature and/or other conditions were present, the same potential for formation of OCS exists where the ratio is the opposite.

To a certain extent, dilution may also be an important consideration. Reactions that proceed in high yield at high concentrations may not proceed at all if performed under dilute conditions.

Examples of the Use of These Principles

Pulp bleaching

A perfect example of the need to provide some supportive evidence of like mechanisms is the insupportable extrapolation of the historical presence of PCDD/F in pulp mill effluents and the suggested formation of OCS. It has been well established that the formation of PCDD/F in pulp bleaching was caused by electrophilic aromatic substitution of the unchlorinated dibenzo-p-dioxin and dibenzofuran (Kringstad et al. 1988; Voss et al. 1988; Berry et al. 1989; LaFleur et al. 1990). This type of ionic chemistry occurs because bleaching is performed in an aqueous environment. Free radical chemistry (as invoked by the Schulman and Klingele *de novo* formation hypothesis) is detrimental to the quality of the pulp; thus, steps are taken to suppress this chemistry. In older bleaching processes, this involved the use of 12 to 15% chlorine dioxide, a free radical scavenger. The active chlorinating agent responsible for the formation of PCDD/F in pulp bleaching is Cl_2. In order to eliminate the potential formation of PCDD/F in bleaching, the US and Canadian pulp and paper industry has moved to the use of chlorine dioxide bleaching processes. The switch to this bleaching chemistry has virtually eliminated all TCDD/F formation, and forms the basis of the NPDES effluent guideline limitation recently promulgated by EPA.

EPA conducted extensive sampling and monitoring of a variety of bleaching processes in the development of their effluent guideline (Federal Register 1998; US EPA 1993). This work included testing for many of the compounds that would provide evidence for other potential OCS mechanisms. Included in these analyses were carbon tetrachloride; tri- and tetra-chloro ethanes and ethylenes; di-, tri-, and hexachlorobenzenes; hexachlorobutadiene; and even styrene itself. EPA found no evidence of the presence of these compounds in the bleach plants they studied. This provides further evidence that the types of high energy free radical chemistry required to form OCS are simply not present in pulp bleaching.

To summarize:

The historical formation of PCDD/F in the bleaching process has been demonstrated to be due to an electrophilic aromatic substitution mechanism, <u>not</u> a high energy free radical mechanism.

Since free radical chemistry has undesirable effects on pulp quality, steps are taken to minimize it.

The pulp industry has changed its bleaching practices to the point where TCDD/F formation is virtually eliminated. These process changes have significantly reduced the incidental formation of other chlorinated organics as well.

EPA's data generated during their development of the pulp and paper industry effluent guideline demonstrate the absence of other indicator compounds that should be present if the *de novo* OCS mechanism was operative.

Taken together, there is no justification for extrapolating from the historical presence of PCDD/F in pulp bleaching to the potential for this process to produce OCS. In fact, the clear understanding of the reaction mechanisms responsible for the presence of PCDD/F in historical bleaching processes is evidence that OCS would not be expected.

Vapor phase degreasing

The Battelle report seems to liken the process of vapor phase degreasing with aluminum degassing. In the case of the aluminum degassing process, the temperatures are above the melting point of aluminum (reported by Battelle as 600°C), and either hexachloroethane or chlorine gas are introduced to force their reaction with hydrogen. Comparing this with solid metal parts at or just below the boiling point of the solvent (e.g., 74°C for 1,1,1-trichloroethane) and inferring a potential for the formation of OCS is not technically sound.

Pesticide manufacture

The Battelle report sites pesticide manufacturing as a potential source of OCS. The discussion seems to involve mostly 2,4-dichlorophenol and products made using it as an intermediate. The process cited in the Battelle report is the controlled chlorination of phenol using a reasonably selective chlorination agent. There is nothing in this process that even begins to suggest the kinds of conditions necessary to produce OCS.

The authors state, "The methods for producing 2,4-dichlorophenol include the direct chlorination of phenol and/or monochlorinated phenol using chlorine or sulfuryl chloride (SO_2Cl_2) with chlorination promoters and stabilizers. In as much as this reaction is known to form CDD/CDFs, it is by analogy, suspected of forming OCS," citing Kirk-Othmer 1996. We have examined the Third Edition of the reference (which is the only edition we had ready access to), and find that the statement that "In as much as this reaction is known to produce CDD/CDFs…" is a very misleading interpretation. Kirk-Othmer noted that polychlorophenols are starting materials for the synthesis of PCDDs and use 2,4,5-trichlorophenol as the starting material for 2,3,7,8-TCDD. There is no indication that chlorination is the mechanism responsible. For a discussion of the currently accepted mechanism for PCDD formation in chlorophenol manufacturing, see the following discussion on pentachlorophenol. Other workers (e.g., Firestone et al. 1972) have analyzed technical formulations of dichlorophenolics and found no dioxin contamination.

Pentachlorophenol (PCP) production

Generally, the incidental formation of PCDDs during pentachlorophenol manufacturing is thought to be due to the strong basic conditions and condensation of the chlorophenolate salts with each other (see US EPA 1980 for discussion of reaction mechanism). The initial condensation forms a polychlorodiphenyl ether, which then undergoes an intra-molecular reaction to form polychloro-p-dibenzodioxin. Since technical pentachlorophenol has significant levels of tetrachlorophenols, the PCDD distribution is predominated by OCDD, followed by varying amounts of HpCDD and HxCDD. Generally, PCDFs are at much lower levels. It is also notable that polychlorohydroxydiphenyl ethers are co-contaminants of PCP (Jensen and Renberg 1972; Jensen and Renberg 1973; Nilsson et al. 1974). This fingerprint or product distribution does not resemble any product distribution associated with known sources of OCS. There is no similarity in the reactions responsible for PCDD formation in PCP manufacturing (which are largely ionic) and the *de novo* high energy free radical chlorination and coupling reaction described by Schulman and Klingele (1985). There is no indication that any of the other OCS precursors are present. Thus, no evidence has been presented or is available indicating that there is any similarity to the mechanism for PCDD formation in pentachlorophenol and any known mechanism for OCS formation.

Estimating an OCS Inventory Based on the Presence of PCDD/F

The Battelle report outlines a series of assumptions around ratios of HCB, PCDD/F, and OCS to develop emission factors, then uses the Oheme et al. (1989) sediment data to develop a numerical ratio for extrapolating PCDD/F data to predict or inventory other OCS sources. As was discussed previously, the fingerprint from the metals refining process studied by Oheme et al. (1989) was specifically noted by the authors to be unique. This is actually data that indicate that one should not use this as the basis of a conversion factor for any source other than other metal refining processes, or perhaps the chlor-alkali process, since it clearly demonstrates that this source is unique. Until a link has been established between OCS and a given mechanism of PCDD/F formation, it is totally inappropriate and counterproductive to the goals of the Binational Toxics Strategy to generate “generic” PCDD/F-to-OCS emission factors to estimate source emissions or to develop an OCS inventory. Thus the entire rationale used in Section 4.2 to establish a cornerstone for developing an OCS source inventory is fatally flawed and should be discarded.

Fate Based OCS Release Rate Estimation

Mr. Robert Bailey has reviewed the premise put forth in the second Battelle report regarding the calculation of OCS/HCB/Dioxin ratios from sediments, and their application to suspected source generation rates. He has found this presentation to be seriously flawed. Estimates of OCS releases to the Great Lakes Basin have been grossly over estimated. His comment follow.

As the Battelle authors found when attempting to compile a report on sources of octachlorostyrene (OCS), there is essentially no direct information available on production and releases of OCS. Their approach was to summarize what information they found on the occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. In addition surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. **The conclusion that OCS may be currently, 1999, emitted in significant quantity in the Great Lakes region is not supported by the available data.** The reported dramatic decreases in most of the observed concentrations over the past 30 years and concurrent and continuing decreases in related chemicals suggest that OCS may be disappearing from sight in the Great Lakes.

Environmental Concentrations

In the Great Lakes and elsewhere the observation of OCS in the environment has been the clue to production and release of OCS from a variety of industrial processes. Sediment cores in Lake Ontario show a peak in the concentration of many chlorinated chemicals, chlorobenzenes, pesticides and OCS around 1960 (Kaminsky and Hites, 1984, Durham and Oliver, 1983)[2]. Since that time, waste disposal as well as production technology have improved with great reductions in the release of these chemicals to the environment. In fact, already by 1981 Durham and Oliver (1983) reported the concentration of OCS in Lake Ontario sediments had dropped by over 95% from its 1960 concentration. Huestis et al. (1996) report an approximately 90% decrease in the concentrations of both OCS and HCB in fish from Lake Ontario between 1977 and 1993. The concentration of OCS in Niagara River suspended sediments has continued to drop during the period of 1990 through 1995 (Niagara River TMP).

Sources of OCS

The major recent (post-1980) sources of OCS in the environment seem to have been landfills which received waste from the old processes (pre-1980) described in the Battelle report. For example, prior to the 1970s landfill in the Niagara Falls area received "taffy tar" containing OCS and many other chlorinated organics from the production of chlorine. However the release of OCS from these old landfills has been and will continue to be reduced by (a) cleaning old storm sewers of accumulated chemicals and (b) diverting the current landfill leachate from the landfills to wastewater treatment (Niagara River TMP). This storm sewer cleaning and landfill leachate diversion to wastewater treatment has been and is an ongoing part of the cleanup of the Niagara River.

A second example of reduced OCS emissions is the cleanup of the Ashtabula River. Emissions of OCS and other chlorinated chemicals into the Ashtabula River have been

[2] For complete description of references see bibliography contained in Appendix II

essentially eliminated and a dredging program is planned to remove contaminated sediments which could spread into Lake Erie (Mahan, 1999).

The formation of trace levels of OCS has been documented for a number of processes where chlorine and carbon are present at high temperatures or in electrochemical reactions (Vogelsang, 1986; Kaminsky and Hites, 1984). In general these processes have not been studied closely for OCS because of its low concentrations. As suggested by Schulman and Klingele, it is logical to attempt to predict OCS emissions from the HCB or PCDD/Fs emissions from a variety of processes. The formation of OCS along with HCB, hexachlorobutadiene and polychlorodioxins and furans (PCDD/Fs) from the successive accumulation of two-carbon units, as proposed by Schulman and Klingele, is easy to accept based on the pyrolysis experiments of Lahaniatis (1989). Similarly, the pyrolysis of hexachloroethane used in degassing of molten aluminum in laboratory experiments by Westberg et al. (1997) and qualitatively confirmed by Vogelsang (1986) is consistent with Schulman and Klingele's proposal. However, the formation of PCDD/Fs seems to have a large surface catalysis component which varies widely under different conditions and may be different for OCS. The variations reported in the mixtures of PCDD/Fs from different processes also introduce a great deal of uncertainty in the ratio of OCS production to that of PCDD/Fs. (Summing the different congeners based on their toxicity to calculate a TEQ adds another layer of uncertainty). HCB is chemically more like OCS so that it may be a better surrogate for estimation of OCS concentrations in the environment. However, neither HCB nor TEQ can be considered a good surrogate for OCS in the absence of information linking OCS to each of the wide variety of processes considered in the Battelle report.

In addition, HCB is formed as a byproduct in some specific reactions in the production of highly chlorinated pesticides such as dimethyl tetrachloroterephthalate. Thus, the use of surrogates such as HCB, in the absence of specific information on emission ratios, must be used for only preliminary, order of magnitude, estimates of OCS emissions. Differences in the environmental degradation rates of OCS and surrogates could also change the observed ratio, especially in old samples, and not enough information is available at present to confidently assign the expected change in ratio.

Estimates of OCS emissions from HCB and PCDD/Fs were made in the Battelle report. However, this author will outline below several defects in the Battelle report's estimates of OCS emissions. The first error was taking the relative concentrations of OCS and HCB in sediments as reflecting their water concentrations without correcting for their different partition coefficients. Also, the Battelle report based its ratio of OCS to TEQ (PCDD/F) solely on data from a study of one river, the Elbe. This author proposes using an alternative study based on 400 sites in the U. S. (Kuehl and Butterworth, 1994).

The use of HCB concentrations in environmental samples as a measure of OCS needs to take into account their different physical properties which affect their partitioning in the environment. Neutral chemicals adsorb on sediments in proportion to their octanol/water partition coefficient, Kow (Karikoff et. al., 1979). The log Kow of OCS is estimated to be

approximately 7.46 from structure activity correlations (SRC online Kow) and the log Kow of HCB, approximately 5.5 (Mackay et. al., 1992). Thus, OCS is estimated to adsorb about 100 times more strongly on sediments than HCB. That is, the concentration of OCS on sediment would be 100 times that of HCB at equal water concentrations.

The OCS/HCB sediment concentration ratio for some sediments are:

Durham and Oliver (1983)	0.15, mean, 1900-1981, Lake Ontario
Oliver and Bourbonniere (1985)	0.11, mean, 1980, 1982, Lakes Huron, Erie
Krieg and Krausch (1993)	0.15, mean, 1985-87, Elbe Estuary
Drouilliard et al. (1996)	0.26, mean, 1996, Detroit River

Thus, the concentration of OCS is estimated to be between 0.01 and 0.001 of that of HCB in the water. Presumably, the relative concentrations of OCS and HCB originally emitted would therefore also be between 0.01 and 0.001.

Atmospheric concentration measurements of OCS and HCB are likely to represent current emission ratios. However, such measurements have not been carried out extensively. Hoff et al. (1992) reported atmospheric measurements of OCS and HCB in 1988-89 in Canada near the shore of Lake Ontario. Unfortunately due to experimental design error, their sampling system did not collect all of the HCB during the summer but still the mean concentrations of HCB were nearly 100 times those of OCS, 54 vs. 0.71 pg/m^3. More recent measurements by Dan et al. (1999) did not detect OCS most of the time. HCB is included in the suite of compounds being regularly monitored in the International Atmospheric Deposition Network (IADN) program in the Great Lakes. Results from this program generally show a substantial and steady decline in atmospheric concentrations of HCB and other chlorinated chemicals since 1991 (Cortes et al., 1998, Hillery et al., 1997).

A factor for estimating the environmental concentration of OCS relative to that of 2,3,7,8-TCDD can be derived from the work of Kuehl and Butterworth (1996) in their survey of fish from nearly 400 sites throughout the United States. They report a mean concentration of 2,3,7,8-TCDD in fish of 13.6 pg/g, which made up 55% of the TEQ and a mean of 1.7 ng/g OCS. Converting the mean TCDD concentration to TEQ gives 25 pg/g TEQ which yields an OCS/TEQ ratio of 1700/25 or 68. Correcting for the increased bioaccumulation factor of OCS, $117x10^6$, vs. TCDD, $9x10^6$ (Battelle report) suggests a concentration factor of 68/(9/117) or OCS = 5.2 TEQ. Using this procedure, the concentration of OCS in the environment, and presumably emissions, would be five times the TEQ concentration. This factor can be compared with the OCS/TEQ factor of 653 used in the Battelle report which was derived from data in the Elbe River. The large number of non-detected OCS concentrations which were included at half the detection limit in the study by Kuehl and Butterworth lead to some uncertainty in the factor of five but this uncertainty is probably less than the overall uncertainty in using such a surrogate for OCS as TEQ.

Larry LaFleur has shown that the one-size-fits-all approach used by Battelle to suggest OCS sources is flawed. Additionally, the errors discussed above in the procedure which they used to establish their ration factors produce erroneous release rate figures. Going

through Table 4 of the Battelle report applying a multiplier of 5 to the dioxin emissions and 0.01 to the HCB emissions yields a different perspective on OCS emissions, about 60 pounds OCS emissions for the entire U. S. versus the 4000 pounds estimated in the Battelle report. Mr. Dan Smith has reviewed OCS levels in the environment and concluded that air deposition is not a significant input vector for the Great Lakes. (See discussion which follows.) Given this finding, out-of-basin sources must be discounted from the 60 pound figure. Once the correct analytical data is used to determine if a source or sector actually releases OCS (or a properly identified and ratioed surrogate), the proper surrogate ratio is identified and applied, the "source" is only included if it is in the Great Lakes Basin, and the continuing operation of the "source" is confirmed, the actual Great Lakes Basin OCS release numbers will be substantially lower, and probably not significant.

The Status and Trends of OCS in the Environment

To confirm the lack of significance of the potential or suggested OCS sources which may remain in the Great Lakes Basin, a review of the status of OCS levels in the environment has been made by Dr. Dan Smith of Conestoga Rovers Consulting. The following analyses reviews his findings regarding the current status and spatial and temporal trends of octachlorostyrene (OCS) in Great Lakes media. These questions were addressed:

- What are current concentrations of OCS in Great Lakes media?
- How have concentrations changed over time?
- How do concentrations vary from place to place?
- What can be deduced concerning current sources and future trends?

Methods: Data on OCS concentrations in Great Lakes media were collected from available sources. Emphasis was placed on analyses of data sets that were extensive and relatively consistent in terms of methods of collection and chemical analyses. While some of the data have been published, most recent data were sought and obtained from various agencies. The Canadian Wildlife Services (CWS) supplied more recent data from that agencies long range monitoring of colonial bird eggs. The Ontario MOE supplied recent data on OCS concentrations spottail shiners from the Niagara River. Unpublished data from MOE's monitoring of water and suspended solids in the St. Clair and Niagara Rivers were obtained from MOE. The USEPA supplied unpublished data on OCS concentrations in Lake Ontario, collected by the EPA.

Temporal trends were analyzed based on the model of first order decline

$$C_t = C_0 * \exp^{(rt)}$$

Where C_t is the concentration at time t, C_0 is the concentration time 0 or the start, and r is the first-order rate constant. First-order decline assumes that proportional rates of decline are constant over time, that is

$$\frac{dC}{C\,dt} = \text{constant}$$

First order decline is the most appropriate model for decline of persistent chemicals in the environment because the fate processes that reduce ambient concentrations (e.g., burial, biodegradation, volatilization, photolysis, and dilution) are themselves first order processes. Because temporal trends are assumed to follow first order kinetics, temporal trends were tested with linear regression analysis after transforming concentrations to the natural logs. This produces the following equation

$$\text{Ln}\,(C_t) = \text{Ln}\,(C_0) + r * t$$

In which all parameters are the same as in the first equation. The existence of a first order decline can then be tested, statistically, with linear regression of log concentration on time of collection. Logarithmic transformation of concentration also tended to normalize residuals, a requisite for the use of parametric statistics.

Because absolute changes in concentrations fall as concentrations fall, first order reactions will always trace a concave up path when plotted on the usual linear XY graph (Figure 1)[3]. The inevitable concave up shape, unfortunately, misleads many viewers into believing that concentrations of orgaonchlorines (OCs) are stabilizing over time. Thus, all temporal trends will be depicted on the semilog scale. Time is plotted on the linear X-axis while untransformed concentrations are plotted on a logarithmic Y-axis (Figure 2). Readers unfamiliar with the semilog scale should be advised of the following. First, equal distances on the logarithmic Y-axis represent equal percentage changes in concentration. Consequently first order declines now trace a straight line (Figure 2), eliminating the optical illusion of stabilization that occurs on the linear XY plot. Secondly, absolute changes in concentration tend to look smaller than when plotted on the linear Y-axis, as shown in Figures 1 and 2. When assessing progress over time, therefore, it is important for the reader to look closely at the Y-axis.

Because percent declines per year are more accessible than first-order rate constants, rates of decline over time will be described in the text below in terms of percent declines as opposed to the first order rate constants produced by the regression analyses.

Results

Gull Eggs from the Great Lakes

The CWS eggs sampling program is the best available data base for determining status and trends of organochlorines in the Great Lakes. Since the early 1970s, CWS has assessed OC concentrations in gull eggs from a number of colonies across the Great Lakes. The positions of the colonies are depicted in Figure 3. The gull egg data are extensive over time and space and have benefited from a relatively consistent sampling and analytical methodology (described in Bishop et al. 1992 and Petit et al. 1994)[4]. Another advantage

[3] Figures appear in Appendix III.
[4] For complete reference citations see bibliography in Appendix IV.

of the gull egg data is that the data are regularly disseminated and available to the Great Lakes research community. Thus, the strengths and limitations of these data are better understood than other Great Lakes data sets (e.g., see Smith 1995a, Stow 1995, Hebert et al. 1996, Hebert et al. 1998).

These data were statistically analyzed (by colony and by Great Lake grouping) to determine whether trends were statistically significant. OCS in herring gull eggs declined significantly ($p < 0.05$) from 1987 to 1998 in eggs from all colonies except three – Leslie Spit and Snake Island on Lake Ontario, and Chantry Island on Lake Huron (Figure 4). In the latter three cases, the regressions were marginally significant (e.g, $p < 0.10$). Moreover, when the data from all colonies on a Great Lake were grouped together, rates of decline are highly significant for each Great Lake.

On average, OCS concentrations in gull eggs from colonies on Lakes Erie, Huron, and Ontario tended to be higher than those from Michigan and Superior (Figure 5), although there was considerable variability between colonies on the same Great Lake (Figure 6). OCS concentrations were only sometimes elevated in gull eggs taken from colonies near historical sources such as Channel Shelter Island on Saginaw Bay, the Fighting Island Colony on the Detroit River, and the colonies on Lake Ontario. On the other hand, OCS concentration from the Port Colborne colony on the eastern Basin of Lake Erie and the Niagara River colony were both quite low despite their proximity to historical sources in the Ashtabula and Niagara Rivers (Battelle 1998). The rates of OCS decline over time among lakes were remarkably consistent, despite intralake variability. By colony, rates of decline varied from about 9% per year at Channel Shelter Island to about 24% per year (Figure 7), both on Lake Huron. However, the rates of decline were not significantly different (ANCOVA, $p > 0.05$) across all Great Lakes colonies, and all colonies tended to decline at an average rate of 18% per year. Concentrations of OCS in most colonies are approaching the detection limit (about 1 ppb) (Figures 5 and 6). Eggs were below the limit of detection at least once between 1995 and 1996 in all colonies except two – the Middle Island colony in Lake Erie and the Channel Shelter Island colony in Lake Huron.

Conclusion: From 1987 to 1998, concentrations of OCS in gull eggs fell significantly and somewhat rapidly, on average about 18% per year (Table 3). The rates of decline did not differ statistically among colonies, and declines were very uniform across lakes and connecting channels. These decreases have reduced the concentrations of many colonies to levels near the limit of detection. Spatially, colonies from Lakes Ontario, Erie, and Huron have similar concentrations. Concentrations of OCS in gull eggs from colonies on Lake Superior and Michigan are similar to each other but lower than from the other Lakes.

Spottail Shiners from the Niagara River and Lake Ontario.

Another very useful long-term database for OC in the Great Lakes is provided by spottail shiners represent These data are the property of the OMOE and the Canadian Government, ana collection and analytical methods are described in Suns et al. (1982, 1993) and Suns and Hitchin (1992). As with the gull-egg data, the spottail-shiner data

benefit from relatively consistent methods over the long term as well as frequent sampling over time and space. However, only the data from the Niagara River were obtainable for this report. OCS concentrations in spottail shiners from the upper Niagara River are only rarely above the detection limit, making temporal trends analyses impossible. However, OCS concentrations in shiners from the lower Niagara River were generally above the limit of detection in the beginning of the sampling period in the mid-1980. When less than detect values are assigned the value of ½ the detection limit, OCS concentrations in the lower Niagara River are estimated to have fallen about 8% per year ($p < 0.05$, Figure 7).

Conclusions: Concentrations in shiners taken from the lower Niagara declined at about 8% per year, falling from about 4 ug/kg in the mid 1980s to less than detection in the mid 1990's.

Lake Trout from Lake Ontario

The Canadian Department of Fisheries and Oceans (F&O) collects lake trout and smelt from each of the Great Lakes on an annual basis. F&O data are not readily available to the public or Great Lakes scientific community, so the quality, methods, and extent of these data could not be ascertained. According to information presented in Huestis et al. (1996), lake trout samples from Lake Ontario are analyzed for OCS. These data show significant ($P < 0.05$) declines, about 10% per year, in OCS over time in Lake Ontario lake trout.

Conclusion. Concentrations of OCS fell significantly, about 10% per year, in Lake Ontario lake trout from 1977 to 1993.
Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Water and Suspended Sediments from the Niagara River

The Upstream/Downstream monitoring group samples water at the beginning and end of the Niagara River, at Fort Erie and Niagara-on-the-Lake. These data, therefore, provide information on water quality conditions in Lake Erie, the Niagara River, as well as information about loading of OCS to Lake Ontario. This is a high quality database with relatively consistent methods over time and very frequent sampling. These data are also regularly published and easily obtainable by the Great Lakes science community.

OCS data were obtained from the Upstream/Downstream sampling group for the period between 1989 and 1995. During this period, water samples were generally taken every week. Whole water samples were divided into aqueous and suspended sediments, and chemical analyses were conducted on these two fractions. Although there are MDLs reported for both fractions -- 0.05 ng/l for the aqueous fraction and 2.7 ng/g of suspended sediment -- concentrations well below the MDL (20% or less of the MDL) are routinely reported. Thus, these reports produce three types of data: estimated concentrations above

the MDL, estimated concentrations below the MDL, and data listed as below the detection limit.

At Fort Erie, at the origin of the Niagara River, 281 aqueous fractions and 285 sediment fractions were analyses[5]. None had a reportable concentration of OCS. Thus, OCS was never detected in 566 analyses representing about 285 water samples. OCS was detected at the mouth of the Niagara River at Niagara-on-the-Lake. For the aqueous fraction, 270 analyses were conducted. Concentrations for the aqueous fraction were 43 times between 1989 and 1991, but not since then. For the adsorbed fraction, reportable concentrations of OCS were detected more frequently concentrations, about 55% of the time. To determine long-term trends, total water concentration of OCS for each sample was estimated in the following manner

$$[OCS]_{total\ water} = [OCS]_{aqueous} + [OCS]_{adsorbed} * [suspended\ solids].$$

Given the large number of analyses below detection, the results of a trends analysis will depend somewhat upon what values are given to unreported values. To insure that trends were real, various values were given to the unreported values for adsorbed OCS: 1/2 the detection limit (1.35 ng/g), 1.0 ng/g, and 0.37 ng/g, the lowest value reported. OCS was rarely reported in the aqueous fraction, so unreported data in the aqueous fraction were set equal to zero.

No matter how non-reported values were treated, OCS concentrations were estimated to have fallen significantly over the period. However, the estimated rate of decrease was dependent upon what values were used for unreported values. OCS concentrations declined by about 40% per year when unreported values were set equal to 0.37 ng/l, but only about 28% per year when unreported values were set equal to 1.35 ng/g, one half the detection limit (Figure 8). Ignoring the aqueous fraction and setting unreported values equal to 1.35 ng/g, OCS concentrations on suspended sediments fell about 21% per year. These analyses demonstrate that OCS concentrations really did decline over this period. However, detecting future declines will become more difficult as more and more analyses yield values below the reporting level.

All of these measured rates of decline are probably faster than the long-term average. Oliver and Charlton measured OCS in the Niagara River several times in the fall of 1982. They found an average OCS concentration of 0.06 ng/l in whole water, which is approximately three times the geometric mean concentrations found in 1989. These two dates trace a 15% per year decline. Similarly, OCS concentrations in the Niagara Bar (discussed below) demonstrate long-term declines of about 14.5% per year.

Conclusion. From 1987 to 1995, OCS concentrations at Fort Erie were always lower than the detection limit in both water and suspended sediments. At Niagara-on-the-Lake

[5] The number of aqueous data points does not equal the number of suspended sediment data point because data for one or the other medium are sometimes, albeit infrequently, rejected because of QA problems.

at the mouth of the Niagara River, OCS was detected at reportable concentrations on a semi-regular basis, especially adsorbed to suspended sediments. OCS concentrations in whole water and suspended sediments fell rapidly over this period, between 21% to 40% per year, depending upon the value applied to unreported values. Based on these data, loading of OCS to Lake Ontario is estimated to have decreased about 70% or more between 1989 and 1995.

Suspended sediments and water from the St. Clair River

MOE monitors water at two points in the St. Clair River, Port Edward at the beginning of the of the St. Clair River and downstream at Port Lambton. The methods are similar to those used in the Upstream/Downstream sampling: sampling on a frequent basis (every two to three weeks), fractionation into an aqueous and sediment fraction, detection limits of 0.05 ng/l and 2.7 ng/g, respectively, and analysts who routinely report concentrations below the detection limit. Of 103 analyses of the aqueous fraction sampled at Port Edward between 1987 and 1996, only 5 samples had reportable concentrations of OCS. These 5 samples averaged 0.02 ng/l OCS. Only two of 111 analyses of suspended sediments had reportable concentrations of OCS.

Reportable concentrations were more frequent downstream at Port Lambton. Of 141 analyses of the aqueous fraction taken between 1987 and 1994, only 7 had reportable concentrations of OCS. However, OCS was regularly reported adsorbed to particles. About 90% of analyses of suspended sediment yielded reportable concentrations of OCS (Figure 9). When unreported concentrations are set equal to one half the detection limit, these data produce a significant decline of about 15% per year.

Conclusions: OCS concentrations have generally been well below the limit of detection at Port Edward at the origin of the St. Clair River. Downstream at Port Lambton, OCS concentrations dissolved in water are also infrequently detected above the detection limit. However, concentrations adsorbed to suspended sediments are generally at reportable concentratons, although these concentrations appear to be falling at about 15% per year over the last decade.

Data for the St. Lawrence River/Outflow from the Lake Ontario

Environment Canada also samples OCS at the origin of the St. Lawrence River. These data are diagnostic of St. Lawrence conditions as well as Lake Ontario. The data are apparently generated using the same general methods as with Niagara River and St. Clair River sampling. Reported detection limits were 0.07 ng/l for water and 2.7 ng/g for the adsorbed fraction. For 85 samples taken from 1989 to 1994, OCS concentrations were reported once in the water column and 11 times in the suspended sediment fraction. All of the reported concentrations were below the detection limits. The eleven concentrations reported for the sediment fraction 0.9 ng/g. The single value reported for the aqueous fraction was 0.01 ng/l, which is $1/7^{th}$ the MDL.

Conclusion. Concentrations of OCS in the headwaters of the St. Lawrence River/outflow of Lake Ontario are infrequently detected at concentrations that can be estimated. Current concentrations are well below the detection limit.

Bottom Sediments from Lake Ontario

Two sediment core samples have been taken from Lake Ontario and analyzed for OCS. Durham and Oliver (1983) took a sediment core in the Niagara Bar in 1981, and core samples from the Niagara Bar were taken in 1995 by New York Department of Environmental Conservation (NYDEC 1996). The two cores showed a consistent pattern (Figure 9). In both cores, OCS concentrations in sediments apparently peaked about 1960 and then declined at about 13.5%.per year (Figure 10). For the NYDEC sample, OCS concentrations in sediments deposited after about 1981 were always below the detection limit, which ranged from about 13 to 6.4 ug/kg.

The yearly declines estimated between 1960 and 1981, when OCS concentrations were above the detection limit, can be extrapolated to the present. Assuming that past rates of decline continued to the present, OCS concentrations in Niagara Bay sediments in the early 1990s should be between 0.5 and 1.0 ug/kg (Figure 8). This projection can be compared to the sediment trap data from the Niagara Bar (Oliver and Charlton 1988) and suspended sediment data from the Upstream Downstream Monitoring of the Niagara River (see section above on the Water Concentrations in the Niagara River). Sediments captured in sediment traps should reflect sediments being laid down during that period. Similarly, OCS concentrations in sediments deposited in the Niagara Bar should be a function of OCS concentrations on suspended sediments at the mouth of the Niagara River, which is the source of most particles settling onto the Niagara Bar.

In both cases, however, concentrations of settling and suspended sediment must be normalized to organic carbon levels similar to those found in bottom sediments to reflect the reduced binding capacity of coarser, less organic sediments that finally settle onto the Niagara Bar. Most recently deposited Niagara Bar sediments are about 3.1% organic carbon (NYDEC 1996). Organic carbon concentrations found in sediment traps were about twice those found in settled sediments (Oliver and Charlton 1988). Thus, sediment trap concentrations were divided by two to normalize for organic carbon (Figure 10). The concentrations measured by Oliver and Charlton fall very near the extrapolation line.

The fraction of organic carbon in Niagara River suspended sediments varies considerably, ranging between about 5% to over 30% organic carbon (Kuntz 1988)[6]. Assuming a geometric mean concentration of 10% would require a correction factor of 3.2 to normalize the suspended sediment to the 3.1% organic carbon of the deposited sediments. When concentrations of OCS on suspended sediments from the mouth of the Niagara River are divided by this correction factor, most recent suspended sediment concentrations

[6] These data were kindly supplied by J. Merriman, Ecosystem Health Division of the MOE.

also fit right on the extrapolation line (Figure 10). This combination of information suggests that OCS loading to Lake Ontario has continued to fall at about the same rate (about 14.5% per year) from 1960 to the present.

Conclusion: As evidenced by OCS concentrations in Niagara Bar sediments, loading of OCS to Lake Ontario apparently peaked in the early 1960s, and has fallen about 14.5 % per year since that time to the early 1980s. when concentrations became too low to be detected. More recent data on settling particles in the Niagara Bar region and suspended sediments in the Niagara River have concentrations similar to those extrapolated from the long-term trends, suggesting that this rate of decline has continued to the present.

Additional Data on Status and Trends. OCS was measured in Lake Ontario water column twice, in 1984 (Oliver and Niimi 1988) and 1996 (EPA, unpublished data). Both samples were taken during spring overturn in open water areas of the Lake and were replicated at several sampling locations. Oliver and Niimi report a mean OCS concentration of 4.7 pg/l in the aqueous phase. For the 1996 EPA sampling, all samples yielded concentrations below the detection limit: roughly 0.5 pg/l in the aqueous phase and 0.2 pg/l in the adsorbed phase. As OCS was not detected in any of the 4 samples (three stations with one station duplicated), it can be assumed that the real OCS concentration was well below the detection limit. A reasonable assumption is that the concentration was ½ the detection limits, or about 0.25 pg/l. Using these two dates only, there was about a 95% decrease in water column concentrations of OCS, or about 22% per year. This observation should be treated with caution. Only two periods were sampled, and the analyses were conducted by different analysts.

Discussion.

The above analysis was limited to straightforward description of observable status and trends of OCS in Great Lakes media. These analyses addressed basic questions of how OCS concentrations have varied in time and space. In the context of the "virtual elimination strategy", there is also the less straightforward question of what spatial and temporal trends really mean. Specifically, can spatial and temporal trends in measured concentrations be used as an indicator of underlying trends in external loading?

The simple answer to this question is "no." The problem with inferring changes in loading from changes in ambient concentrations is twofold. First, measured concentrations in many media are often not good indicators of in-lake inventories, especially when measurements are limited. Second, for systems at non-steady-state with external loading, trends of in-lake inventories may be based largely upon internal fate processes and have little or nothing to do with trends in external loading (Endicott et al. 1992a,b, Smith , under review.) With respect to the first problem, concentrations of organochlorines in biota (lake trout, gull eggs, spottail shiners) are known to respond to a number of other factors in addition to abiotic concentrations and levels of external loading. These factors, which confound interpretation of observed trends, include winter weather, prey availability, aquatic prey chain length and structure, terrestrial vs. aquatic foraging,

limnological factors, and potential effects of inter-lake migration (Rasmussen et al. 1990, Rowan and Rassmussen 1992,; Smith 1995a,b, under review; Hebert et al. 1995; 1998) Concentrations of chemicals in the water column and sediments are confounded by sampling error and actual variability due to storms and mixing events as well as long-term changes in lake trophy and suspended sediments concentrations.

In view of the confounding factors affecting organochlorine concentrations, caution should be exercised when extrapolating observed trends, over time and space, in any of the media above to underlying trends in in-lake inventories, and from there, to trends in external loading. This is especially true of inferences based on small data sets and short time trends. For example, consider the OCS data for gull eggs from Lake Ontario (Figure 11). The long-term trend from 1987 to 1998, which shows a significant decrease in OCS concentrations over time, actually consists of three short-term trends: concentrations tended to remain constant from 1987 to 1993, fell precipitously, about 90%, from 1993 to 1995, and then rebounded somewhat from 1995 to 1998 (Figure 11).

Several factors suggest that none of these short term trends is responding to underlying changes of in-lake inventories levels or external loading of OCS. For example, the initial period of stable concentration is more likely attributable to one of the confounding factors affecting organochlorine concentrations in gull eggs (e.g., food chain effects and/or the weather effect). This is apparent because most of the organochlorines also show stable concentrations from the period 1987 to 1993 (Smith 1995a). The organochlorines have disparate sources of external loading to Lake Ontario, and it is not reasonable to expect that the loading of the different external sources of different organochlorines would be synchronized. The short-term pattern of stable OCS concentrations in gull eggs is also inconsistent with data from Niagara River loading. The Niagara River should be the primary external source of OCS to Lake Ontario. Loading of OCS from the Niagara River declined rapidly, from 70 to 80% at the same time that gull egg concentrations remained constant (Figure 8 vs. Figure 11). With respect to the precipitous decline of OCS concentrations from 93 to 95, it is highly unlikely for OCS inventories in Lake Ontario to fall much more than 10% per year, even under condition of complete zero loading (e.g., see Endicott et al. 1992a).

On the other hand, more reliable indicators of trends in ecosystem inventories, but not necessarily external loading, can be obtained by focussing on long-term trends and by looking for similar trends among different media. Despite potential problems with any one data set, there is a high degree of certainty that OCS concentrations have really been falling over the period from 1980 to at least the mid-1990s in Lake Ontario. As summarized in Table 3, there are statistically significant and quantitatively substantial declines in all of the following media:

inflowing Niagara River water concentrations (1989 to 1994)
spottail shiners residing in that inflowing water
in-lake water column concentrations (1994 to 1996, two dates only)
gull eggs (1987 to 1998)

lake trout (1977-1993)
in-lake sediments (1960 to 1981 or 1994 if suspended sediment data can be included).

Similarly, we can be reasonably certain that OCS concentrations in the St. Clair River/Detroit River are also actually declining, because OCS concentrations are declining in the water column, gull eggs. Data on temporal trends in other Great Lakes areas are mostly limited to gull eggs. This might be problematic, except that OCS levels are falling at all of these other colonies, suggesting that OCS inventories are indeed declining in the Great Lakes. Equally important, Lake Ontario and the St. Clair/Detroit River are two of the three areas in which OCS levels are elevated. With the exception of Saginaw Bay, where OCS is also elevated in gull eggs, temporal trends in other Great Lakes areas are of less importance because levels in most media are already near or at the detection limit.

Keeping in mind the limitations of the data, the following addresses the questions posed at the beginning of this discussion.

- **What are current levels of OCS in Great Lakes media?**

As shown in Table 2, current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes. The notable exceptions to this are OCS concentrations in lake trout in Lake Ontario. Extrapolating past rates of decline (about 10% per year) onto early 1990's concentrations (about 30 ug/kg in whole raw lake trout) suggest that whole raw lake trout will continue to exceed the current detection limit (1ppb) till about 2025. It is also likely that OCS is above the detection limit in fish from the other Great Lakes, and potentially the St. Clair/Detroit River and Niagara River. Assuming a relatively constant relationship between gull eggs and fish, it is likely that OCS would be about as high in Lake Erie and Lake Huron fish as in Lake Ontario. OCS might also be detectable in very large lake trout from Lake Superior and Lake Michigan.

- **How have levels changed over time?**

In all media with adequate data, levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year (Table 3). Rates of decrease over time are generally highly statistically significant, quantitatively substantial, and consistent across media, time, and space. It can be concluded with a high degree of certainty that OCS concentrations in the Great Lakes have declined dramatically over the last two decades.

- **How do concentrations vary over space, i.e., from place to place?**

Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lake Erie and Huron. Elevated concentrations appear

to be related to historical sources in Saginaw Bay, the St. Clair River, and Lake Ontario. Data from other media are limited, but tend to support the spatial trends found in gull eggs.

- **What can be deduced concerning current sources and future trends?**

The available data suggest that atmospheric sources were probably never an important source of OCS to Great Lakes ecosystems. Gull eggs colonies with elevated concentrations are generally downstream of historical sources of OCS in Saginaw Bay, the St. Clair River, and the Niagara River. Concentrations of OCS in gull eggs from colonies on Lake Michigan and Lake Superior, which are far away from historical sources, tend to be about about 3 to 4 times lower than those downstream of suspected historical sources. It is also important to note that concentrations of OCS in gull eggs from all of the colonies are fallin at about the same rate in all Lake groupings (Figure 5). This observation is inconsistent with the hypothesis of significant current atmospheric inputs, as one would expect atmospheric dependent sites to decline at a different rate than colonies primarily affected by past and current riverine and point sources. The rapid decreases in OCS concentration in gull eggs and the other media also suggest that current atmospheric loading is relatively insignificant and allows unimpeded declines of OCS in the lakes. Consistent with all of these observations, OCS is rarely if ever detected in air monitoring near the Great Lakes (Dann 1997).

If atmospheric loading of OCS can be assumed to be negligible, that leaves current external loading from point and non-point sources and internal loading from sediment inventories of past external loading. It is critical to differentiate between internal and external loading. External sources are generally controllable and likely to yield some benefits if controlled. Sediment inventories, on the other hand, are not readily easily controlled and will remediate naturally without further action.

The two different sources should produce different patterns over time and space. Systems whose OCS concentrations are tightly controlled by external sources should have very site specific and unique temporal patterns, because external source control will be a site-specific function of regulatory commitment, local economic conditions, amenability to control, and other site specific factors. Thus, if, as is often hypothesized, sites on the Niagara River are a major current source of OCS to the Lake Ontario, one would expect declines in OCS in the Niagara River and Lake Ontario media to be episodic, tied tightly to specific remediation activity. It is also expected that the temporal patterns of decline will be very different from OCS declines at other sites, and very different from declines of other chemicals with similar fate processes (e.g. PCBs and DDE) not associated with sources of OCS.

The patterns of decline for systems controlled by internal sediment stores are likely to be very different. As the fate processes controlling declines in sediments are relatively constant across time and space and across PTS chemicals, one would expect systems controlled by internal inventories to decline at fairly similar rates through time, and across

lakes and across PTS chemicals. The data, while limited, seem more consistent with the latter hypothesis. The very similar declines of OCS in the gull eggs across colonies suggests some common mechanism of decline (e.g, fate processes affecting sediment inventories.)

Great Lakes system dominated by internal sediment inventories should also have orderly declines of different persistent toxic substance. That is, concentrations of different organochlorines should decline in a predictable fashion based on the vulnerability to fate processes affecting concentrations in the sediments. More volatile and degradable chemicals like hexachlorobenzene should dissipate faster from the Great Lakes than more stable, less volatile chemicals such as Mirex and dieldrin. PCBs are of intermediate vulnerability and should dissipate with an intermediate speed. The predicted rates of relative decline for internal inventories of various organochlorine can be estimated from the model of Endicott et al. (1992a) under a condition in which external loading was reduced to zero. In this case, long-term declines of these chemicals depends on vulnerability to various loss processes. These estimated zero-loading declines can be compared to yearly declines observed for lake trout in Lake Ontario (Huestis et al. 1986). As can be seen from Figure 12, there is a significant relationship between predicted and observed declines of different organochlorines (regression analysis, $p < 0.05$). That is, as predicted, the different organochlorine are declining in a significantly orderly process, further supporting the hypothesis that external loading is unimportant. It is also important to note that OCS is actually declining faster than predicted. At the least, this graph demonstrates that OCS, which has received little regulatory attention in the last several decades is declining considerably faster than compounds like DDT, PCBs, and TCDD, which have been under very strict regulation. This observation is inconsistent with a system dominated by external sources, which ought to be more controllable.

There are other data to substantiate that current concentrations of OCS in Lake Ontario are based on internal sediment inventories as opposed to current external loading. Loading from the Niagara River can be estimated from the Upstream/Downstream monitoring. Best estimates of early 1990s loading from the Niagara River are about 4.3 to 6 grams per day, depending upon what values are assigned to non-detection data. According to Endicott et al, model, this loading of OCS should produce lake trout concentrations of about 5.2 to 3.8 ug/kg in whole lake trout. These predicted values are 6 to 8 times lower than observed concentrations for this period, about 31 ug/kg (Huestis et al. 1996). The discrepancy between observed and predicted concentrations also supports the hypothesis that OCS concentrations in Lake Ontario are largely due to internal sediment inventories, as opposed to current external loading.

Table 2. Summary of results. Decreases are based on regression analyses. ND means not detected.

Medium	Location	Time Frame	Decrease (% per year)	Most recent conc.
Gull egg	Lake Ontario	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Erie	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Huron	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Superior	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Michigan	1987-1998	Yes (20%)	Some ND
Gull egg	Niagara River	1987-1998	Yes (17%)	Some ND
Gull egg	Detroit River	1987-1998	Yes (20%)	Some ND
Spottail Shiner	Lower Niagara River	1985 -1995	Yes (8%)	100% ND
Spottail Shiner	Lake Ontario	1985 -1995	NA	100% ND
Lake Trout	Lake Ontario	1977-1993	Yes (10%)	0 % ND
Water	Niagara River	1989-1995	Yes (16%-21%)	50% ND
Water	Upper Niagara River	1989-1994	NA	100% ND
Water	Lake Ontario	1984, 1996	Yes (20%)	100% ND
Water	St. Clair River (Port Edward)	1989-1996	Yes (15%)	>95% ND
Water	St. Clair River (Port Lambton)	1989-1995	NA	10% ND
Water	St. Lawrence	1989-1996	NA	90% ND
Sediments	Lake Ontario	1960-1981 (95)	Yes (12%)	100% ND

CGLI appreciates the opportunity to provide these comments. We look forward to working with the Workgroup to correct the process and technical errors represented by the Battelle report.

Sincerely,

George H. Kuper, President
and CEO

Appendix I

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Critical Review of Battelle Report
Dr. Larry LaFleur

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Appendix III

Figures 1 - 12

Status and Trends of OCS In Great Lakes Media

Figure 1. First order decline (10% per year decrease) on linear XY plot

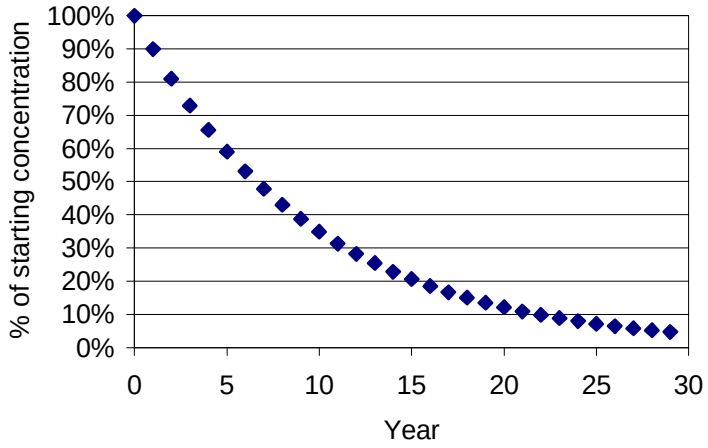

Figure 1. A first order decline graphed on the more usual linear XY plot.

Figure 2. First order decline (10% per year decrease) on semi-log XY plot

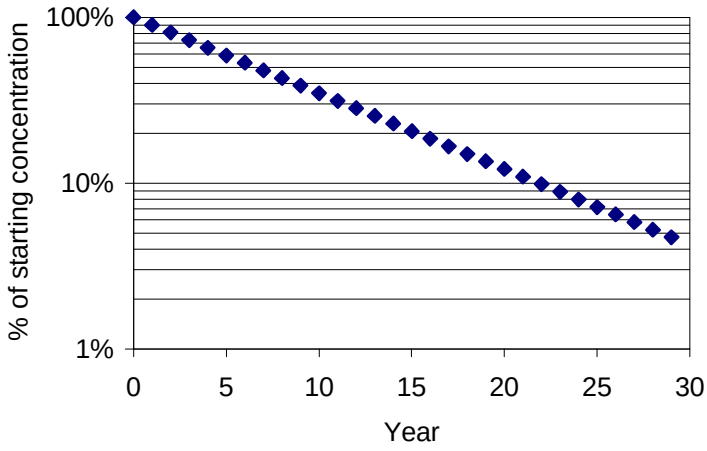

Figure 2. The same first order decline plotted on semi-log paper.

Figure 3. Location of Herring Gull colonies on the Great Lakes.

Figure 4. Yearly % Decline vs. Colony

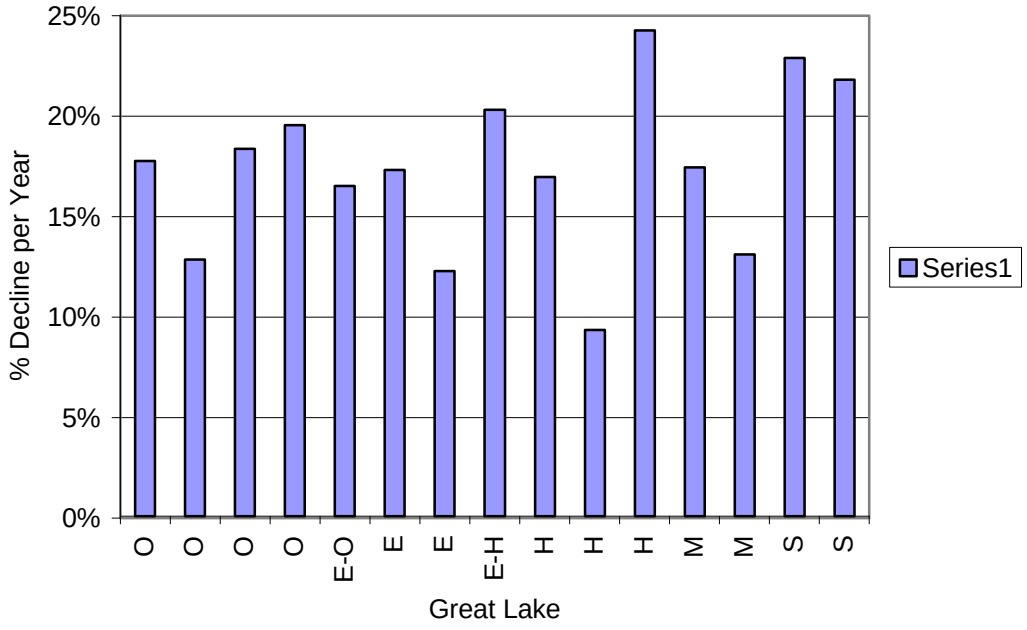

Figure 4. Best-fit % declines per year estimated from linear regression. Colonies are plotted in the following order which generally follow an east-west gradient: Lake Ontario colonies in the order of Strachan Island, Snake Island, Leslie Spit, Hamilton Harbor, Niagara River, Lake Erie colonies in the order of Port Colborne and Middle Island, Detroit River, Lake Huron colonies in the order of Channel Shelter Island, Chantry Island, and Double Island, Lake Michigan colonies with ?/ and ??, and Lake Superior colonies Agawa Rock and Granite Island.

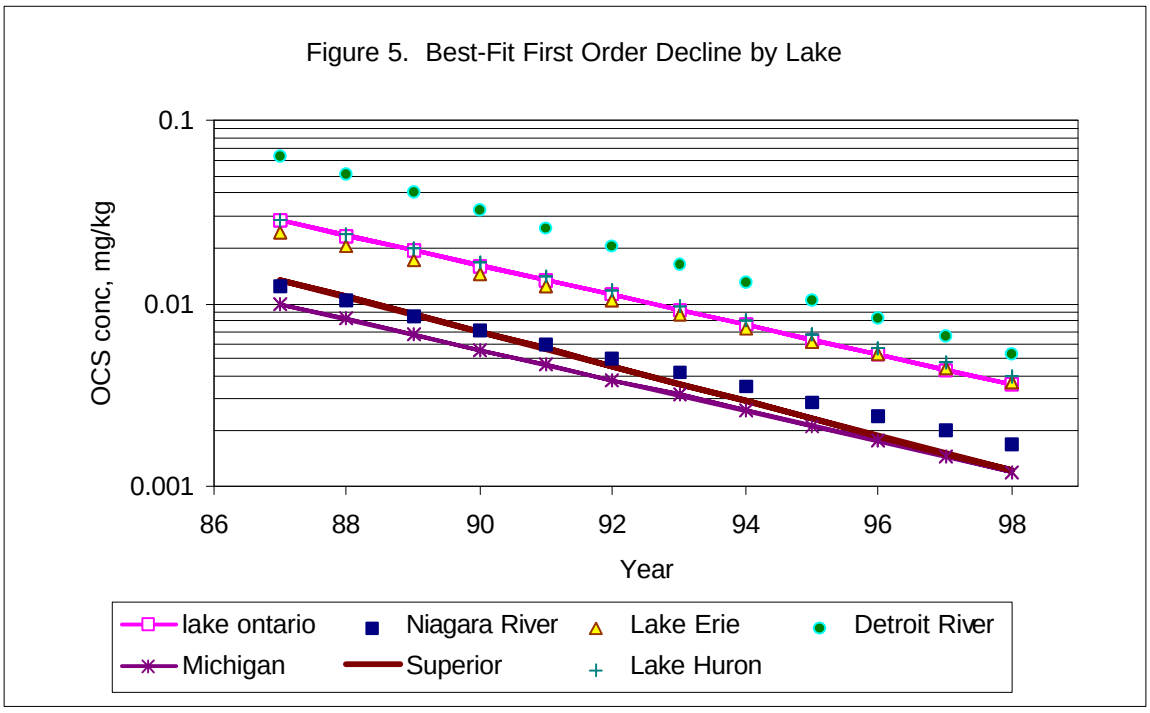

Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Figure 6. Mean OCS (94-98) versus Lake

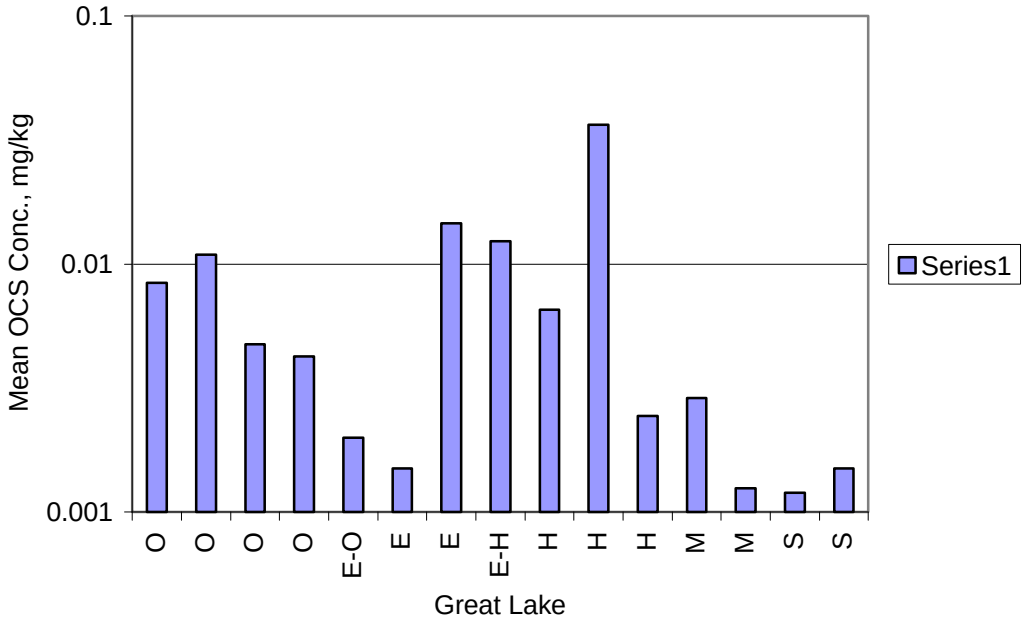

Figure 6. Most-recent (1994 to 1998) concentrations of OCS by colony. Sequence of colonies same as in Figure 6.

Figure 7. OCS in Spottail Shiners in Lower Niagara River (MOE Data)

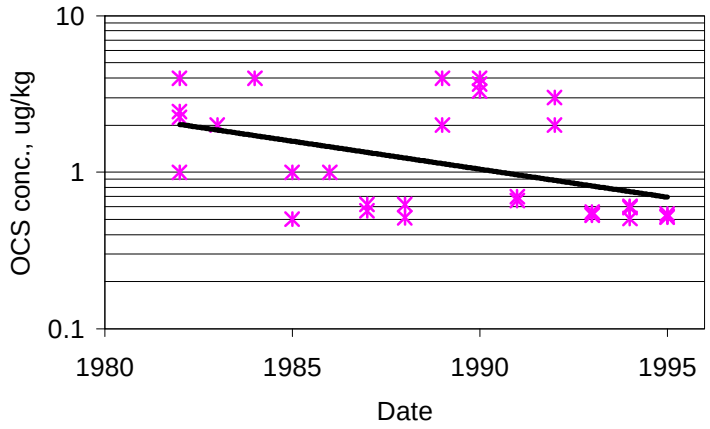

Figure 7. OCS concentrations in spottail shiners from the lower Niagara River. Values less than detection limit (1 ug/kg) set equal to 0.5 ug/kg. Some data points have been altered somewhat (e.g., 10% to 20%) to aid viewing when more than one sample on the same date had the same concentration.

Figure 8. Estimated whole water concentrations of OCS at Niagara-on-the-Lake

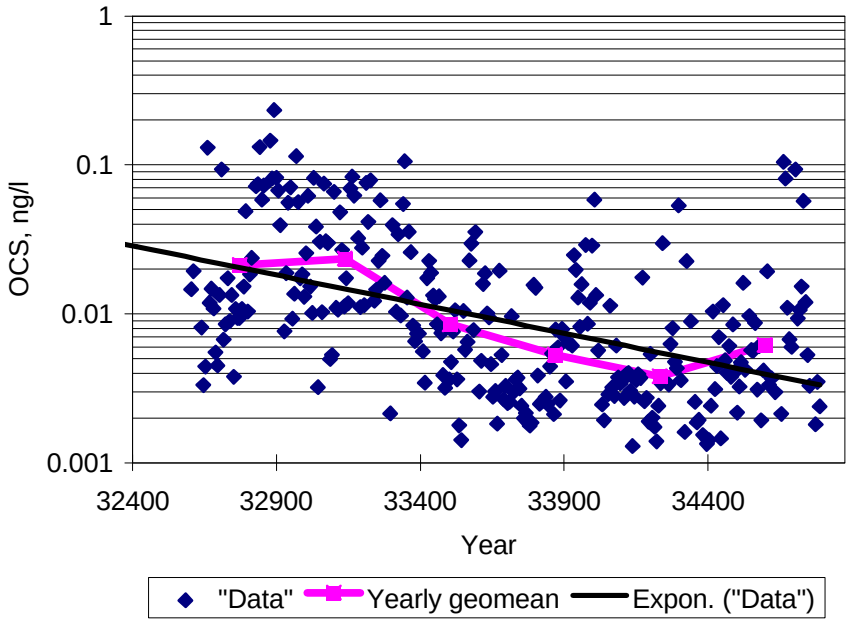

Figure 8. Concentrations of OCS in Niagara River water at the mouth of the Niagara River.

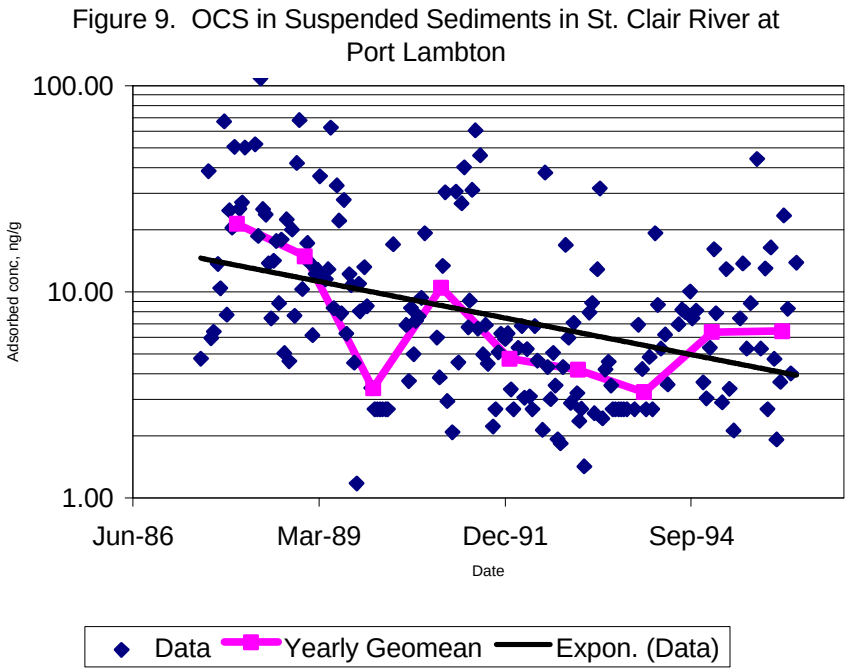

Figure 9. Concentrations of OCS on suspended particle from the St. Clair River at Port Lambton.

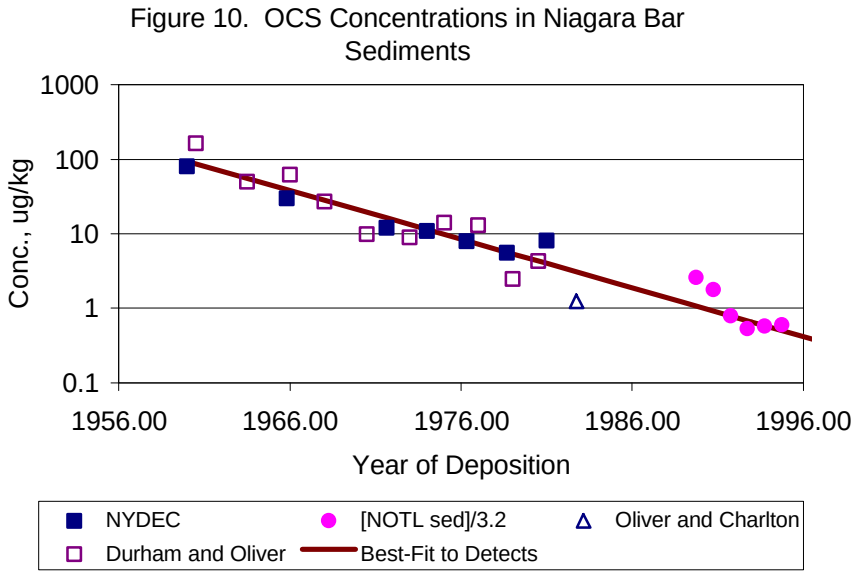

Figure 10. Concentrations of OCS in sediments from Lake Ontario. For the NYDEC sample, all analyses for sediments deposited between 1981 and 1995 were below the detection limit, but these data are not depicted on this graph.

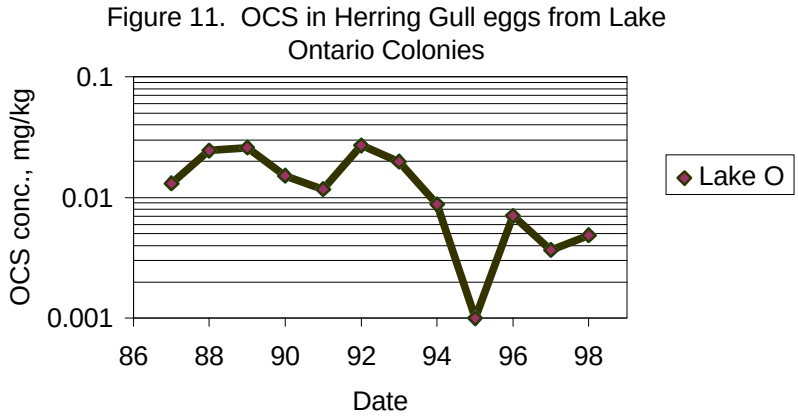

Figure 11. Mean concentrations of OCS in gull eggs from the four Lake Ontario gull egg colonies (Strachan Island, Snake Island, Leslie Spit, and Hamilton Harbor.)

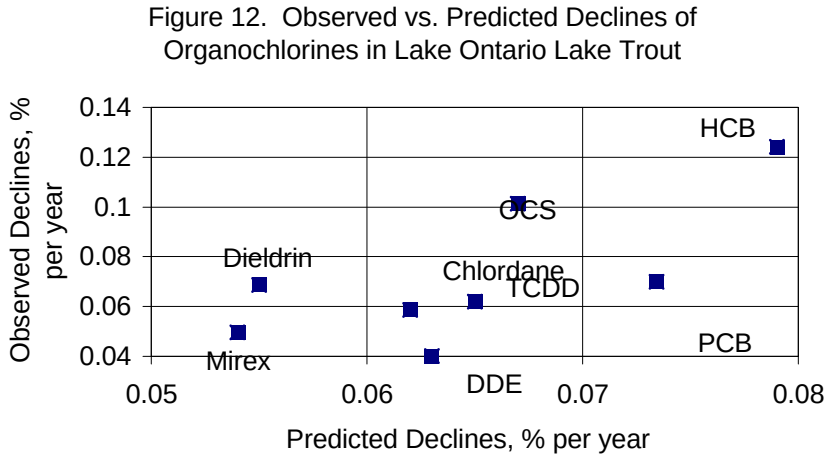

Figure 12. Observed versus predicted declines of different organochlorines in Lake Ontario lake trout. Predicted rates of decline (per year) from the Endicott et al. model (1992a) after cessation of loading. Observed rates are best-fit declines observed in lake trout, data from Huestis et al. (1996).

Appendix IV

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March 1, 1999

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Mr. Darryl Hogg
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Ministry of Environment
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Dear Darryl and Frank:

The Council of Great Lakes Industries (CGLI) is pleased to submit our report regarding octachlorostyrene (OCS) releases, to the Great Lakes Binational Toxics Strategy (BNTS) OCS Workgroup. It represents the combined efforts, and extremely hard work, of many. It addresses suggested industrial sources of OCS on a sector-by-sector basis, provides a review of OCS levels in the environment, discusses OCS formation mechanisms, assesses the environmental fate of the substance, and evaluates the use of HCB and dioxin surrogates for estimating OCS release inventories.

Much of the sector-by-sector information has been provided by industry contacts. Many of these contacts have submitted some or all of this information separately to either U.S. EPA Region 5 or Environment Canada. Others have chosen to funnel their information through CGLI via this report. Our agreement with information providers has been that we will forward the information which they provide, to the governments on an anonymous basis. For that reason, the sector review section of this report contains few references. CGLI will gladly direct any questions which the governments or Workgroup members may have back to the appropriate parties to facilitate discussion on the few issues which may remain.

The OCS environmental status section is an extremely important and telling portion of this report. It shows that this material is disappearing from the Lakes at very high rates, faster than any other organochlorine. This decay rate (8 to 30% per year) demonstrates that any remaining OCS sources are insignificant. This work also highlights the importance of

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environmental fate and mass balance assessments as a means for assessing virtual elimination progress for priority chemical substances.

The report examines the practice of using surrogate relationships (HCB and dioxin releases) to estimate OCS release rates when source specific OCS data is not available. The conclusions are that these relationships are very process specific and should not be used unless the exact case-by-case ratio is known or determined experimentally.

It is notable that the OCS release elimination or reduction progress reported in the sector-by-sector review section was accomplished through a range of measures. Some processes have been shutdown, some modified, and others outfitted with additional or enhanced treatment technologies. This success demonstrates the multi-pathway options which are available and can produce virtual elimination outcomes.

Finally, the comprehensive nature of this report reflects the special circumstances regarding OCS, relative to other Level I substances on the BNTS list. Little source information regarding OCS is in common circulation. Industry personnel, prior to the CGLI information request effort, had not looked closely at the release of this specific substance. Because OCS has not been a "main stream" substance in regulatory circles, because the material is disappearing rapidly from the Great Lakes ecosystem, and in light of the attempts which have been made by the Battelle OCS report and newly drafted Canadian OCS inventory document to estimate releases on the basis of surrogates, a special effort was needed provide the proper perspective regarding this material.

We look forward to continuing our work towards successful implementation of the BNTS and would be pleased to answer questions regarding this report. You may direct them to me, Werner Braun (703) 741-5815 (werner_braun@cmahq.com), or Dale Phenicie (770) 487-7585 (dkphenicie@mindspring.com).

Sincerely,

George H. Kuper, President
and CEO

cc: Gary Gulezian
Liz LaPlante
Ron Shimizu
Alan Waffle

Octachlorostyrene
and
Suggested Industrial Sources

A report to the
Great Lakes Binational Toxics Strategy
OCS Workgroup

March 9, 1999

Council of Great Lakes Industries
3600 Green Court, Suite 710
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Acknowledgments

This report was produced by the Council of Great Lakes Industries (CGLI), through the greatly appreciated hard work of many people in industry who voluntarily provided their time and effort toward the success of the Binational Toxics Strategy. The information contained, regarding octachlorostyrene (OCS) releases to the Great Lakes, was acquired through a multi-Industry/multi-company participative effort requiring hundreds of conversations, meetings with many industrial groups and organizations, and responses to information requests and questionnaires.

The report was prepared by Dale K. Phenicie (Environmental Affairs Consulting), with assistance from Werner Braun (V.P. of CGLI and U.S. co-chair of the CGLI OCS Working Group), Don Hames (Dow Canada and Canadian co-chair of the CGLI OCS Working Group), Bob Redhead (Robert J. Redhead Ltd.), with contributions from representatives of CGLI member companies, many others within industry, and representatives from U.S. and Canadian industry trade associations. These efforts have provided the important picture regarding industrial process use and OCS release potential within the basin.

Special contributions were made by Dr. Daniel W. Smith of Conestoga Rovers Consulting, Mr. Robert Bailey or Bailey Associates, and Mr. Larry LaFleur of the National Council of the Paper Industry for Air and Stream Improvement. Their in-depth presentations have provided insights into OCS formation and release chemistry as well as the state of OCS concentration in the Great Lakes ecosystem.

Partial financial support for the production of this report was provided by grants from U.S. EPA and Environment Canada.

Requests for copies of this report, or questions, should be directed to Mr. George Kuper, President and CEO, Council of Great Lakes Industries, PO Box 134006, Ann Arbor, MI 48113-4006, (734) 663-1944, FAX (734) 663-2424, e-mail:ghk@cgli.org.

This report and additional information regarding industry efforts towards implementation of the Great Lakes Binational Toxics Strategy can be found on the CGLI Website at *http://www.cgli.org.*

Octachlorostyrene
and
Suggested Industrial Sources

A report to the Great Lakes Binational Toxics Strategy
OCS Workgroup

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Octachlorostyrene
and
Suggested Industrial Sources

A report to the Great Lakes Binational Toxics Strategy
OCS Workgroup

Executive Summary

As part of the Great Lakes Binational Toxics Strategy (BNTS) Octachlorostyrene (OCS) Workgroup effort to evaluate sources of octachlorostyrene and meet Strategy challenge goals, the Council of Great Lakes Industries (CGLI) has committed to:

- coordinate an industry review of suggested industrial sources of OCS,
- determine if these sources do exist within the Great Lakes Basin,
- if so, determine their status, and
- seek reduction commitments for significant sources.

This report provides a status report on the work begun to evaluate suggested sources.

The Study Approach

The approach to the OCS source review work was to:

- study information regarding suggested industrial sources and the basis for selecting them,
- review this information with knowledgeable persons within each sector, and
- provide perspective and reality check for the significance of potential sector releases through examination of OCS environmental concentration trend data.

The Findings

This work has produced the following findings.

- In many industry sectors, pollution prevention measures have eliminated or significantly reduced OCS releases.
- In other sectors, Great Lakes Basin located processes which had previously released OCS have been shut down.
- In a few sectors, continuing OCS releases, if they actually occur at all, are at very low, often not detectable, levels.
- The examination of OCS environmental trend data shows that concentrations are decreasing rapidly. They are at or approaching detection limits in most media. If remaining OCS sources were significant, it would be expected that environmental concentration trends would be reaching a plateau, or in the worst case scenario, increasing.

The Conclusions

Based on the sector by sector analysis results and environmental trend data described in this report it is concluded that, for the sectors for which we have data, contemporary industrial sources of OCS in the Great Lakes ecosystem have been virtually eliminated1.
This status has been achieved through exercise of pollution prevention and pollution control measures.

The CGLI OCS Inventory Matrix

CGLI's initial efforts to collect source information were based on the Battelle Memorial Institute prepared Draft Action Plan for OCS (January 1998). To provide a guide for a source information gathering effort, a spreadsheet or Work Sheet matrix was constructed by CGLI and presented to the OCS Workgroup. Following publication of the second Battelle OCS report (November 5,1998), it was revised to include some of the additional source information presented in that report. As is evident upon examination of the revised OCS Work Sheet, substantial information was required from many industrial sectors. The status of this effort is discussed in this report, sector by sector.

The OCS Suggested Source Decision Tree

Upon examination of the expanded suggested source picture presented by the second Battelle report, CGLI determined that a decision process would be needed to determine how to proceed with the pursuit of release reductions which will lead to attainment of the BNTS OCS challenge goals. This conclusion led to the recognition that if the technology was not in use within the industry or the Great Lakes Basin, no further information pursuit was necessary. Extending the logic through a stepwise thought process led to the decision tree which is explained and used in this report.

Canadian Inventory Efforts

The Ontario Section of Environment Canada has undertaken an effort to construct an OCS inventory for the Province. Like the second Battelle report it makes use of HCB/OCS ratios to calculate OCS releases. This approach is problematic, as is discussed within this report. However, unlike the Battelle report, the Ontario inventory project has made use of a decision tree-like process and relied on the existence of specific industrial processes within the Province as the key to whether or not OCS releases from that sector occur. Consequently, the February 17, 1999 draft inventory report concludes that "[s]everal suspected sources of OCS have been

1 The primary focus of this study has been the Great Lakes Basin. However, also included in this report is information pertaining to the likelihood of OCS releases at St. Lawrence River watershed based (Quebec) magnesium production and copper recycling (electronic equipment) facilities. Emissions potential at both was found to be unexpected or small.

eliminated…" In addition, the report corrects reports that OCS may have been released from sectors such as the pulp and paper industry and rubber tire manufacturing.

Industry Sectors Contacted

Based on the sectors listed on the CGLI OCS Inventory matrix, contacts were identified and initiated. Information received ranges from OCS specific details to acknowledgment of receipt of information provided by CGLI and a commitment to follow-up and provide a response. The sector by sector review information presented in the report is summarized below.

Chlor-alkali Production:

The suggested source of OCS release from Chlor-alkali production is graphitic electrode process use. The Chlorine Institute is unaware of any U.S. chlor-alkali facilities that still use graphite anodes. The process is, likewise, no longer in use in Ontario.

Magnesium Production:

Magnesium industry personnel contacted by CGLI, in both the U.S. and Canada, have confirmed that graphitic magnesium production processes are used in a plant in Becancoeur, Quebec. A new plant, which will also use an electrolytic process, is under construction in Asbestos, Quebec. It will employ pollution control equipment which will limit potential releases of OCS to the environment to very low levels.

PVC Incineration:

The assertion in the Battelle report that incineration of PVC materials represents a source of OCS is based on laboratory experiments which were designed to demonstrate that OCS could be formed. The report does not take into account the fact that incinerators are operated using combustion controls which avoid conditions favoring formation of dioxins and related compounds. The draft Canadian inventory report relates that OCS concentrations at the one municipal incinerator tested were not detected.

Metal Degreasing:

Chlorinated solvents have, for many years, been used to remove oils, greases, and other contaminants from metal parts. The draft Battelle report offers no data to support the contention that this process is a source of OCS, instead the report relies on the tenuous comparison to the aluminum degassing process. Most degreasing processes do not provide sufficient energy to facilitate the series of reactions necessary to produce OCS and are therefore inappropriately implicated. The report also fails to consider the fact that chlorinated solvent waste generated in the boiling sump of a vapor degreaser is subject to strict storage, handling, and disposal requirements under the U.S. hazardous waste regulations and therefore not released into the ecosystem.

Auto Fuel Combustion:

The Canadian Petroleum Products Institute has conducted a study which concluded that OCS is not present in tailpipe emissions or petroleum fuels.

Aluminum Production (Pri./Sec.):

Representatives of the aluminum industry report that hexachloroethane (HCE), alleged to produce OCS as a by-product, is no longer used in most primary aluminum degassing operations. No smelters in the Great Lakes Basin use HCE. Chlorine is used instead. The industry knows of no association between the use of this process and the production of OCS. No electrolytic processes are in use in the U.S.

PVC Coated Wire Recycling:

Vinyl Institute personnel have confirmed that open burning of wire for copper recovery is no longer an industry practice. As mentioned in the Battelle report, insulation is mechanically removed from scrap wire before recycling. Testing at a Quebec facility recycling electronic scrap found no significant releases of dioxin or styrene.

PVC Polymerization/Production:

The Vinyl Institute (VI) has no data showing that OCS is formed during the polymerization of vinyl chloride monomer (VCM). Although the report is not clear in this regard, it appears that EPA's speculation that PVC production is a source of OCS stems from an assumption that OCS is formed when polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F, or "dioxin") are formed, and that dioxin is formed during the polymerization of vinyl chloride. The VI does not believe that dioxin is formed during the polymerization process, and this conclusion is supported by the findings in the Vinyl Institute Dioxin Characterization Program Phase I Report (August 1998), which was previously submitted to EPA.

Pesticide Manufacture:

The practice of assuming a relationship between HCB presence and OCS presence in the pesticide manufacturing sector (or any other for that matter) should only be done when enough information is available to correctly determine the ratio on a case-by-case basis. Conditions which may produce HCB may or may not also produce OCS, or do so at differing ratios. In addition, it is inappropriate to base conclusions on HCB releases from pesticide manufacture or use on the basis of regulatory limits. Actual product HCB concentrations are significantly lower than maximum content limits set by registration authorities.

Pentachlorophenol Production/Wood Preservation:

The Pentachlorophenol Task Force, an industry group which provides data needed for continued registration of "penta" in the U.S., Canada and elsewhere, has no information confirming the

presence of OCS in "penta," as is suggested in the Battelle OCS report.

Pulp and Paper Making/Chlorine Bleaching:

Pulp and paper mills are not thought to produce OCS or HCB. Details are provided by the industry. They conclude that pulp and paper making processes "have never favored formation of highly chlorinated substances." OCS and HCB are, of course, very highly chlorinated materials. Conditions do not favor their formation in pulp mills. The draft Canadian inventory report confirms that OCS production which may have been associated with graphitic electrode based chlor-alkali production facilities is not now occurring. The process is no longer used in Ontario. The one on-site chlor-alkali facility operating at a Great Lakes Basin U.S. pulp and paper mill makes use of the diaphragm cell process and does not use graphite anodes.

Chlorinated Solvent Production:

Chlorinated solvent production does appear to have been a source of OCS contamination in the past. The draft Battelle report does not attempt, however, to evaluate changes in the manufacturing process over the last 10 to 15 years. As a result, the report bases its conclusions about potential releases from solvent manufacture on practices that are no longer applicable. Today, waste products from solvent production are either reused in other processes, incinerated, or placed in secure landfills, keeping them out of the ecosystem. Additionally, many of the facilities and processes from which the older OCS release data is cited have been shut down.

Coke Production:

Test results from Stelco Inc.'s Lake Erie Steel Company failed to detect OCS in coke oven emissions. Environment Canada has determined that the iron and steel sector is not a source of OCS and that an error had occurred in 1990 reporting activities which had suggested otherwise.

Tire Manufacturing:

Industry contacts explain that the assertion that tire tread compounds contain HCB (from which OCS suggested releases were calculated) comes from an April 98 report by U.S. EPA. It is based on analysis of tire tread compound which the industry has since found to have been reported in error. Additionally, EPA has historically reported the presence of chlorine in natural rubber. The industry has found no evidence that rubber contains chlorine.

Other Sectors:

CGLI is currently seeking information regarding these sectors:

- ***Chlorinated Solvent Incineration***
- ***PCB Incineration - Waste Oil Burning***
- ***Rare Metals Production***

The Status and Trends of OCS in the Environment

A review of OCS levels in the environment has been made to determine the significance of potential or suggested OCS sources which may remain in the Great Lakes Basin. The following questions were posed, data was studied, and conclusions reached:

- What are current concentrations of OCS in Great Lakes media?

Answer: Current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes.

- How have concentrations changed over time?

Answer: Levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year.

- How do concentrations vary from place to place?

Answer: Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lakes Erie and Huron. Elevated concentrations appear to be related to historical sources.

- What can be deduced concerning current sources and future trends?

Answer: From atmospheric date, it appears that long range transport may be a vehicle for deposition of OCS in the Great Lakes ecosystem. However, based on the environmental trend data presented, this source is probably not significant.

Additional data are presented to substantiate the hypotheses that current concentrations of OCS are primarily based on internal loading from sediment inventories, based on previous loading. Sediment inventories are exhaustible and inexorably declining. Current external loading of OCS from sources within or outside of the Great Lakes basin are insignificant.

A Critical Review of the Second Battelle Report

OCS Formation Considerations:

The National Council of the Paper Industry for Air and Stream Improvement has studied the mechanics of chlorinated phenolic compounds extensively. Their review of the draft Battelle report has concluded that from a mechanistic and scientific process standpoint, the document is seriously flawed. A detailed analysis is provided.

Additional analyses have been conducted by Dr. Daniel W. Smith of Conestoga Rovers Consulting, and Mr. Robert Bailey on behalf of the Chlorine Chemistry Council. They have concluded that the primary Battelle approach was to summarize what information they found on occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. Data from one and two decades ago are presented as if these data reflected current levels and current sources. In depth trends analyses presented in the discussion which follows demonstrate that OCS concentrations are falling, at a half-life rate of between 3 to 7 years. In addition, surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. The draft conclusion that OCS may be

currently emitted in significant quantity in the Great Lakes region is not supported by either the current analyses for OCS in the environment or correctly calculated emission estimates based on surrogates.

Octachlorostyrene
and
Suggested Industrial Sources

A report to the Great Lakes Binational Toxics Strategy
OCS Workgroup

Introduction

As part of the Great Lakes Binational Toxics Strategy (BNTS) Octachlorostyrene (OCS) Workgroup effort to evaluate sources of octachlorostyrene and meet Strategy challenge goals, The Council of Great Lakes Industries (CGLI) has committed to:

- coordinate an industry review of suggested industrial sources of OCS,
- determine if these sources do exist within the Great Lakes Basin,
- if so, determine their status, and
- seek reduction commitments for significant sources.

This report provides a status report on the work begun to evaluate suggested sources.

The starting point for this work was the January 1998 Draft Action Plan for Octachlorostyrene prepared for the workgroup, at the request of U.S. EPA Region 5 personnel, by Battelle Memorial Institute. Sources suggested in the Draft Action Plan were categorized and logged into a spreadsheet matrix to serve as a road map for tracking down information regarding industry sectors, processes, and individual companies to determine release status.

To determine the basis for the listing of Action Plan suggested sources, literature references used to support the January 1998 paper were requested from Battelle. Copies of the papers were obtained and reviewed1.

Just prior to the November 16, 1998 Chicago Binational Toxics Strategy Stakeholders meeting, a second Battelle report was released by U.S. EPA Region 5. It included a new, much expanded, list of literature references and suggested additional industrial sources2. It made use of an

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1 Of the 18 original references, half of them did not pertain to OCS production or release. It is unclear why these references were chosen. They do not appear to be relevant. Of those references which do pertain to OCS, three draw conclusions regarding releases by extrapolating backwards from sediment data, two report results from laboratory combustion studies deliberately designed to produce chlorinated off-gases, two of these report the identification of compounds emitted tentatively as OCS, and one demonstrated OCS release potential from aluminum processing through laboratory experiments. Only one paper actually reports a documented OCS release. In that case, a landfill leachate test proved positive for OCS while a concurrent effluent sample did not.

2 The second Battelle report includes a list of 107 references which are said to pertain to the release and/or environmental fate of OCS. Of the 107, nine are those which were included in the original list of 18 and which do pertain to OCS. The 9 irrelevant references have been screened out. However, given the nature of the original references (the fact that only one actually documents a release), the new longer list must be examined carefully. Some or several may not substantiate actual OCS release activity. CGLI has requested assistance from Region 5 and Battelle personnel in locating copies of the references.

assumed relationship between hexachlorobenzene (HCB) and OCS releases. If HCB releases had been detected from given sources, OCS was assumed to have also been released. Attempts were made to quantify OCS releases on the basis of sediment calculated release factors.

This report provides a status report on the work begun to evaluate suggested sources from the first OCS report, the Draft Action Plan. The source list has been updated somewhat on the basis of clarifying information contained in the second Battelle report. However, the additional sources, especially those which appear to be theoretically based and depend on HCB or other chlorinated compound associations have not, at this time, all been added to the CGLI OCS source matrix.

In addition to the original Battelle Draft Action Plan, Environment Canada has produced an OCS inventory as part of their reporting activities supporting the Canada-Ontario Agreement (COA). This report also addresses sources listed in the COA report.

The CGLI OCS Inventory Matrix

To serve as a guide for identification of source information gathering, a spreadsheet or matrix was initially constructed by CGLI and presented to the OCS Workgroup. It listed the suggested sources as described in the Draft Action Plan. Contact points were established for each of the suggested sources and provided opportunities to record reference data, release information, and reduction commitments. Upon review of the second Battelle OCS report, CGLI revised the matrix. The suggested source categories were sectorized and specific sector processes upon which OCS releases had been based or suggested were included. This refinement was made to expedite industry contact and information gathering. The revised source matrix appears in Appendix I.

The revised matrix utilizes the decision tree information gathering and source management concept. This approach, described below, will simplify the assessment of the suggested sources and focus efforts and attention on those which are significant from the standpoint of meeting the BNTS OCS challenges. Decision information for sectors for which data has been collected has been included in the Appendix II presentation.

As is evident upon examination of the revised OCS Work Sheet, substantial information must still be obtained from many industrial sectors. This data collection effort is, and has been, underway for some time. The status of this work is discussed, sector by sector, below.

The OCS Suggested Source Decision Tree

Upon examination of the expanded suggested source picture presented by the second Battelle report, CGLI determined that a decision process would be needed to determine how to proceed with the pursuit of release reductions which will lead to attainment of the BNTS OCS challenge goals.

The decision tree approach derived is shown in Appendix II. The basis for this approach came from the fact that both of the Battelle reports are based on very old reference information. Papers and assessments of industrial process dating to the 1980's are used to draw conclusions regarding documented OCS releases or theoretical OCS production. Industry has been in the process of phasing out older technologies. Therefore, it was determined that a logical first step is to determine if a technology which has been linked with OCS production is still in use. This conclusion led to the recognition that, if the technology was no longer in use within the industry, no further information pursuit was necessary. Likewise, if the technology is in use but not in the Great Lakes Basin, further pursuit may not be necessary. Extending the logic through a stepwise thought process led to the decision tree.

Canadian Inventory Efforts

The Ontario Section of Environment Canada has undertaken an effort to construct an OCS inventory for the Province. Like the second Battelle report it makes use of HCB/OCS ratios to calculate OCS releases. This approach is problematic, as is discussed within this report. However, unlike the Battelle report, the Ontario inventory project has made use of a decision tree-like process and relied on the existence of use of specific industrial processes as the key to whether or not OCS releases from that sector occur. Consequently, the February 17, 1999 draft inventory report concludes that "[s]everal suspected sources of OCS have been eliminated, including the production of chlorine, chlorinated solvents, vinyl chloride/ethylene dichloride/PVC, pentachlorophenol, and pesticides. These were eliminated largely because such operations are not conducted in Ontario."

In addition, the report corrects reports that OCS may have been released from sectors such as the pulp and paper industry and rubber tire manufacturing. While much more extensive review of this new draft report is needed, especially relative to the use of surrogate ratios for release quantity estimates, the approach of concluding that Basin "sources" do not exist when the technology is not practiced within a sector or the Basin is the correct one. Also, these inventory reviews should "correct the record" when evidence is available showing that "sources" have been named in error.

Industry Sectors Contacted

Based on the sectors listed on the CGLI OCS Inventory matrix, industry contacts were identified and initiated. A listing of the sectors contacted appears in Table 1. The table indicates sectors targeted for contact in both Canada and the U.S. It also indicates which contacts have resulted in responses. In some cases, the responses are preliminary and follow-up information will be forthcoming. In only a few cases, the correct point of contact has not yet been established. We are continuing to pursue these contacts and report on them when the needed information has been collected.

Table 1

Industry Sectors Contacted Regarding OCS Release Information

Sector	Canada	U.S.	Response Received	
			Canada	U.S.
Chlor-alkali Production	X	X	X	X
Magnesium Production	X	X	X	X
Vinyl Production	X	X		X
Oil Recycling	X	X		
Auto Fuel Production	X	X	X	
Auto Fuel Use	X	X	X	
Chlorinated Solvent Production	X	X	X	X
Aluminum Production (Pri/Sec)	X	X	X	X
Pesticides Manufacture	X	X	X	X
Pesticides Use	X	X	X	X
Wood Preservation		X		X
Pulp and Paper Manufacture	X	X	X	X
Coke Production	X	X	X	X
Waste Disposal - Incineration	X	X		
Cement Kiln Recycling	X	X		
Tire manufacturing	X	X		X

Sector Responses

As mentioned above, most sector contacts have provided responses. As noted in Table 1 and at the end of this section, a few sectors have not yet reported back to CGLI. These responses will be forwarded to the Workgroup when received.

One common response has been that OCS releases have not been previously associated with the suggested industry sectors or processes, and little or no data is available. In addition, MACT regulations are currently under development for VOCs as a class, but not for individual compounds. MACT standard development data is commonly collected for aggregated VOC compounds, not specific compounds such as OCS. Sector contacts are researching databases and emissions reports for additional information.

A sector-by-sector summary of the information obtained so far is provided in the paragraphs which follow.

1 Chlor-alkali Production:

The suggested source of OCS releases from Chlor-alkali production is graphitic electrode process use. The Chlorine Institute is unaware of any U.S. chlor-alkali facilities that still use graphite anodes. The Institute relates that the use of these anodes was common prior to the advent of metal anodes. Contacts with individual producers confirm that these conversions have been made. In fact, many were done during the late 1960's. By the late 1980's all conversions are believed to have been accomplished. One incentive for completing the conversions was a significant cost savings over the older graphite electrode process. The process is, likewise, no longer in use in Ontario. Using the decision tree concept. It is not necessary to pursue OCS releases from graphitic electrode chlor-alkali production facilities any further since the technology is not in use.

"Questions" regarding carbon containing membrane cell chlor-alkali production processes, raised in the second Battelle OCS report are of the "theoretical" nature. There are substantial differences between the electro-chemistry of a diaphragm cell utilizing graphite anodes vs. the chemistry in the membrane cell process. Suggestions that OCS may be produced just because carbon may be present is a substantial stretch. There has been no confirmation that OCS is produced in these cells.

2 Magnesium Production:

Magnesium industry personnel contacted by CGLI have confirmed that no graphitic processes are currently used in the Great Lakes Basin. One such facility is located in Becancoeur, Quebec, in the St. Lawrence River watershed. Another is under construction in Asbestos Quebec.

An environmental assessment was conducted on the proposal to build the Asbestos plant. Chlorine will be evolved in the electrolysis stage where chlorinated hydrocarbons (CHCs) will also be generated. The gas will be used to regenerate hydrochloric acid which will collect most of the

CHCs. Air emissions of dioxins and furans from the facility are expected be 0.09 g/y TEQ. CHC levels in the leach residue will be controlled by carbon adsorption from the return acid. The residue will contain approximately 20 g/y TEQ at a concentration of 66 pg/g TEQ and will be stored in a secure impoundment. All pond water will be returned to the process which will have no liquid discharge to the environment. Carbon filter material will be sent to an off-site hazardous waste facility for disposal by incineration.

OCS is included in the environmental monitoring program for the facility. While there can be no assurance that there will be no OCS releases, it is anticipated that the CHC control measures will limit potential releases of OCS to the environment.

A Utah based producer is currently evaluating dioxin and/or HCB release potential from their graphitic operation. State of Utah environmental agency personnel are participating in the study. The generation or release of OCS has not been a concern at this facility and is not a part of this study.

3 PVC Incineration:

The assertion in the Battelle report that incineration of PVC materials represents a source of OCS is based on laboratory experiments which were designed to demonstrate that OCS could be formed. The report does not take into account the fact that incinerators are operated using combustion controls which avoid conditions favoring formation of dioxins and related compounds. The draft Canadian inventory report relates that OCS concentrations at the one municipal incinerator tested were not detected.

The Battelle report suggests that PVC products that are land-disposed rather than recycled or incinerated can be potential sources of OCS if accidental landfill fires occur. At the same time, the report indicates that all incineration processes involving chlorinated substances should be expected to form OCS. Studies on dioxin emission from commercial incineration systems indicate that the control of combustion conditions is the most effective way to minimize dioxin emissions.[3] It is reasonable to conclude that this technology would also be effective in the mitigation of OCS emissions. Further, modern landfill management practices mitigate the potential for landfill fires.

4 Metal Degreasing:

The Halogenated Solvents Industry Alliance, Inc. has reviewed the portion of the Battelle report which suggests that OCS may be released by metal degreasing operations. Their response to this assertion is:

> Chlorinated solvents have, for many years, been used to degrease oils, greases, and other contaminants from metal parts. In the typical process, the solvent is heated to its boiling point and the contaminants are flushed by the solvent vapors as they condense on the part

3 *See, e.g.,* "The Relationship Between Chlorine in Waste Streams and Dioxin Emissions From Waste Combustor Stacks," H. Gregor Rigo, *et al.*, American Society of Mechanical Engineers (1995).

in the vapor zone. To ensure effective cleaning, contaminants are periodically removed from the boiling sump and disposed of as hazardous waste.

In its discussion of metals degreasing, the draft report suggests that:

> As in aluminum degassing, the reaction of chlorinated solvents with carbon deposits on the metal at elevated temperatures *may* generate OCS as a byproduct in the contaminated solvent drained from the machine or in the organic impurities that accumulate in the sump. (*emphasis added*)

The draft offers no data to support this contention, instead relying on the tenuous comparison to the aluminum degassing process. In the information provided for degassing, however, the draft notes that the production of OCS has been found to occur at 600° C. As indicated previously, the temperatures routinely encountered in the sump of a vapor degreasing are around the boiling point of the solvent (121°C or less). Clearly, the degreasing process does not provide sufficient energy to facilitate the series of reactions necessary to produce OCS. Even in a poorly maintained degreaser, where contaminated sludge has accumulated on the heating coils in the boiling sump and temperatures may rise above the boiling point, safety controls required on the equipment shut off the heat supply well below the temperatures encountered in aluminum degassing.

The report also fails to consider the fact that chlorinated solvent waste generated in the boiling sump of a vapor degreaser is subject to strict storage, handling, and disposal requirements under the nation's hazardous waste regulations. These wastes may not be discarded in a landfill and generally are destroyed in hazardous waste incinerators or cement kilns. To the extent that destruction of degreaser wastes may contribute to release of OCS, the report already addresses them in its consideration of incineration processes.

5 Auto Fuel Combustion:

The Canadian Petroleum Products Institute, through its National Toxic Substances Task Force (TSTF) carried out an extensive worldwide survey and assessment of "chemical emissions from vehicle tailpipes." This two phase study consisted of a detailed literature search of all known vehicle tailpipe emission databases. Phase 1 of the study was completed in 1997 with the report published in November 1997. Phase 2 is currently being completed. Octachlorostyrene was not detected in any of the studies, and the experts concluded that it would be very unlikely to find the substance in tailpipe emissions. Discussions with refinery experts also confirmed that the substance is unlikely to be found in petroleum products.

6 Aluminum Production (Pri./Sec.):

Representatives of the aluminum industry report that hexachloroethane (HCE) is no longer used in most primary aluminum degassing operations. Additionally, no smelters in the Great Lakes Basin use HCE. Chlorine is used instead. The industry knows of no association between the use

of this process and the production of OCS. However, as part of a MACT rule development study, the quantity of chlorine used for this purpose has been reduced to control chlorine, HCl, dioxin and furan releases from the process. If OCS were produced, these process changes would also result in lower releases of all volatile compounds, including any OCS which might be present. New MACT standards for these sources are expected to be finalized by U.S. EPA by December 31, 1999. A three year compliance period will be provided, assuring that the sought after reductions will have been made by year 2003. Many facilities control volatile emissions through use of lime injected baghouses. This equipment is expected to further reduce releases.

A separate primary MACT standard, which became final in 1997, addresses Particulate aromatic organic matter. A three year compliance period will produce PAOM reductions of at least 50%. The only Great Lakes Region facility, a State of New York plant, is "fast tracking" PAOM MACT reductions. All other facilities in the region use a "prebake" process which produces much lower PAOM emissions.

The secondary aluminum industry is also subject to new MACT standards. These standards require that old cans be delacquered before melting. In addition to the new standards, the industry has moved away from direct melting practices because of low recovery experience.

Any estimate of OCS releases from the aluminum sector must consider the impact these changes have had, and will have, on final quantities.

Finally, Aluminum Industry personnel have related that no electrolytic processes are in use in the U.S.

7 PVC Coated Wire Recycling:

Vinyl Institute personnel have confirmed that open burning of wire for copper recovery is no longer an industry practice. As mentioned in the Battelle report, insulation is mechanically removed from scrap wire before recycling.

Investigations at a Quebec[4] primary copper smelting facility which recycles electronic scrap was tested for dioxin, furan, and styrene emissions. At plastic feed rates four or five times normal production rates, dioxin/furan releases did not exceed 0.1 grams TEQ per year. Styrene was not detected in an acidic waste stream which would have concentrated the material at detection limits ranging from 0.01 to 6 ug/l.

This sector does not appear to produce significant quantities of OCS.

4 This facility located in Northwestern Quebec would be unlikely to influence environmental quality with the Great Lakes Region, but monitoring results may be of relevance in assessing potential releases from copper smelters.

8 PVC Polymerization/Production:

The Vinyl Institute (VI) has no data showing that OCS is formed during the polymerization of VCM[5]. Although the report is not clear in this regard, it appears that EPA's speculation that PVC production is a source of OCS stems from an assumption that OCS is formed when polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F, or "dioxin") are formed, and that dioxin is formed during the polymerization of vinyl chloride. The VI does not believe that dioxin is formed during the polymerization process, and this conclusion is supported by the findings in the Vinyl Institute Dioxin Characterization Program Phase I Report (August 1998), which was previously submitted to EPA.

The OCS Report states that the formation of OCS in the PVC polymerization process "is not certain". From a chemistry perspective, we have no reason to believe that any perchlorinated species are created in the vinyl chloride polymerization process. Thus, the report's conclusion should be revised to state that OCS is not predicted to be formed during the polymerization process.

9 Vinyl Manufacturing Process

Likewise, OCS formation would not likely occur in the ethylene dichloride EDC cracking process for the manufacturing of vinyl chloride monomer (VCM). If OCS is formed as a minor, inadvertent, byproduct in the VCM process, its formation would likely occur further downstream. As acknowledged in the report, OCS is not deliberately manufactured, and the vinyl industry does not use OCS in any form. Further, based on knowledge and experience, any OCS that is unintentionally manufactured would be captured in the EDC or VCM purification process and/or emission control devices, which are strictly regulated under the Clean Air Act (CAA), Clean Water Act (CWA), and the Resource Conservation and Recovery Act (RCRA) to control emissions of hazardous air pollutants and other substances. As the OCS Report itself notes that "[t]here are no emissions released directly to the atmosphere [from EDC and VCM production facilities], as regulations require emission sources to be enclosed and all emissions to be collected." Report at 41 (emphasis added).

As the report notes, gaseous streams are treated by incineration and liquid streams and wastewater are stripped of trace organics. In this regard, it is also important to note that incineration at EDC/VCM facilities, as well as PVC production facilities, is highly regulated and subject to continuous emissions monitoring. The incinerator operating parameters at these facilities provide a high degree of assurance. Further, the trace organics stripped from wastewater are typically routed back into the production process or to a well-controlled incinerator.

Because the industry has little or no releases of OCS, the VI has not developed data on emissions of OCS from the vinyl manufacturing process. However, a worst case estimate can be

5 VI's members include: Borden Chemicals and Plastics Limited Partnership, CertainTeed Corporation, CONDEA-Vista Company, The Dow Chemical Company, Formosa Plastics U.S.A., The Geon Company, Georgia Gulf Corporation, Kaneka Delaware Corporation, Occidental Chemical Corporation, PPG Industries, Inc., Shintech, Inc., Union Carbide Chemicals and Plastics, and Westlake PVC Corporation.

constructed based on industry data and the OCS/dioxin ratio presented in the report. Please note that we have no basis to support the ratio factor of 653 for OCS to dioxin described in the report.[6] Report at A-4. We use that figure here only to support the conclusion that the report should state that the vinyl industry is not a source of OCS.

If we assume that a relationship between the formation of dioxin and the formation of OCS in the EDC/VCM/PVC process exists, we can begin by basing an emissions estimate for OCS on dioxin emissions. In its August 1998, Dioxin Characterization Phase I Report, the vinyl industry indicated that the only potential release points of dioxin in the PVC manufacturing process were the incineration of the vinyl chloride recovery process vent, emissions from the polymer dryers, and wastewater. The recovery process vent is regulated under the CAAs National Emission Standards for Hazardous Air Pollutant Emissions (NESHAP) to comply with a 10 parts per million (ppm) VCM emission limit in the vent stream.[7] For EDC/VCM production, dioxins were found in emissions from the process vent incinerators and wastewater, which are also regulated.

The report should note that the production of 12.5 billion pounds of PVC and 13.6 billion pounds of VCM from 25.5 billion pounds of EDC per year generates less than 31.3 grams on a Toxic Equivalent (TEQ) basis per year of dioxins to air and less than 0.22 grams TEQ/year of dioxins to water. As noted above, although we have no basis to support the ratio factor of 653 for OCS to dioxin that is described in the OCS Report, OCS emissions based on the suggested ratio of OCS concentrations to dioxin emissions can be estimated. Applying the ratio factor, total U.S. EDC/VCM/PVC production would emit less than 20.4 kilograms per year (kg/y) of OCS to the air and less than 0.143 kg/y of OCS to water. In addition, these would be *total* national release numbers and would not reflect actual releases or deposition in the Great Lakes basin. The VI study found that over 98 percent of estimated dioxin releases originated from facilities that manufacture EDC/VCM or EDC/VCM/PVC, which, as noted above, are not located in the Great Lakes region. In sum, given EPA's estimate of 4,157 pounds (1,890 kg) per year emissions of OCS, the calculated worst case for the EDC/VCM/PVC industry contribution is so small as to be inconsequential.

Finally, members of VI are responsible for the majority of the domestic production volume of EDC, VCM, and PVC. However, the vinyl industry has a limited presence in the Great Lakes Basin. All production of EDC and VCM in the U.S. occurs in Kentucky, Louisiana, and Texas. EPA itself acknowledges that there are no EDC/VCM production facilities in the Great Lakes Basin. Report at 53. In addition, more than 90 percent of U.S. PVC production occurs outside of the Great Lakes states. Indeed, the report only identifies a single location for PVC polymerization in the Great Lakes Basin. (Report at 54) **This facility has been closed**. EPA is also considering the potential for atmospheric deposition to be a source of OCS contamination in the Great Lakes Basin. However, EDC, VCM, and PVC production facilities are geographically located such that atmospheric deposition in the Great Lakes is so unlikely that it is reasonable to

6 The lack of an asserted correlation between a specific dioxin/furan congener and OCS adds further uncertainty to the OCS/dioxin ratio. This is particularly important since the small amounts of dioxin and furans produced in the EDC/VCM manufacturing process predominantly are the more highly chlorinated, less toxic species, such as octachlorodibenzo-p-dioxin.

7 40 C.F.R. Sec. 61.60 *et. seq.*

conclude that the industry is not a source of OCS in the Great Lakes region. This conclusion is supported by the history of OCS contamination in Lake Ontario sediments and in Lake Ontario trout. The report reflects decreasing OCS levels, approaching the near-zero level between 1921 and 1981. Report at 20. Similarly, concentrations of OCS in trout declined from 263 nanograms per gram in 1977 to 31.3 ng/g in 1993. During these periods of declining OCS releases to the environment, U.S. production of EDC, VCM, and PVC increased substantially to more than 25, 13, and 12 billion pounds a year, respectively. If the EDC/VCM/PVC industry was a source of OCS in the Great Lakes Basin, this would have been reflected in actual monitoring data.

10 Pesticide Manufacture:

The practice of assuming a relationship between HCB presence and OCS presence in the pesticide manufacturing sector (or any other for that matter) should only be done when enough information is available to correctly determine the ratio on a case-by-case basis if such a ratio exists, and if so, what it might be. Conditions which may produce HCB may or may not also produce OCS, or do so at differing ratios. (For details see Critical Review of Battelle Report presentation provided below.) However, since OCS data are not available, the following surrogate information is presented.

HCB can be produced as a trace byproduct in many reactions where chlorine and carbon are present. Thus, it has been produced as a waste product from the production of many chlorinated chemicals. In the USA and Canada, this waste is either incinerated or placed in secure underground facilities. None of the facilities listed in the US Toxics Release Inventory which release HCB are located in the Great Lakes region.

HCB has been present as a microcontaminant in some chlorinated pesticides. Manufacturers have made process and raw material changes which have dramatically reduced or eliminated HCB concentrations. EPA regulates the maximum concentration of HCB possibly present in the pesticides as shown in Table 2. Current manufacturing methods produce materials with average HCB concentrations well under those listed in Table 2.

For example, atrazine producers confirm that HCB levels in their product are nearly always not detectable. One producer explains that “the average HCB level for a typical production campaign is < 1 ppm.” “[T]he maximum hexachlorobenzene content found in atrazine technical was 9.7 ppm….” Therefore it would be wrong to assume that chlorinated contaminants are present in pesticides at their respective regulatory levels. This information, the fact that pesticides are not applied as “neat” material straight from the drum, in consideration of the declining application rates now used for pesticide products, all lead to the conclusion that contaminant levels resulting from pesticide production or use are not significant.

Table 2.
Regulatory Levels for HCB as a Contaminant in Pesticides

Product	Maximum HCB concentration
Dimethyltetrachloro-terephthalate	1000 ppm
Atrazine	40 ppm
Simazine	40 ppm
Picloram	50 ppm
Pentachloronitrobenzene	500 ppm
Chlorothalonil	40 ppm
Lindane	100 ppm

11 Pentachlorophenol Production/Wood Preservation:

The Pentachlorophenol Task Force (PTF), an industry group which provides data needed for continued registration of "penta" in the U.S., Canada and elsewhere, has no information confirming the presence of OCS in penta, as is suggested in the Battelle OCS report. Comprised of the two U.S. registrants of penta, Vulcan Chemicals and KMG-Benuth Inc., the PTF is committed to ensuring that regulatory decisions regarding penta are based on sound science and reflect current, up-to-date-data.

Page 50 of the draft Battelle report states that the production of penta is suspected of forming OCS as a byproduct in trace amounts. A citation to Kirk-Othmer 1996 is given in support of that statement. The authors of the Battelle report attempt to draw a parallel between PCDD/PCDF formation during penta manufacture and OCS formation. Indeed, Table 4 in the draft report goes so far as to suggest that the amount of penta used annually to treat utility poles may contain up to 16,325,000grams of OCS. Based on roughly the 17 million pounds of penta being produced annually by PTF member companies, the figure in the Table would translate to an OCS content in penta of approximately 0.4 percent.

As indicated above, PTF members have no information confirming the presence of OCS in penta, as suggested in the second draft Battelle report. Nonetheless, we fail to see the scientific rationale for drawing a connection between the formation of trace quantities of certain higher chlorinated PCDDs/PCDFs during penta manufacture with any possible OCS formation. PTF members have examined the Kirk-Othmer reference and fail to see how it supports the contention of the report. Moreover, the suggestion that penta contains up to 0.4 percent OCS is plainly wrong. PTF member Vulcan has analyzed its penta for the presence of any contaminants at levels above 0.1 percent and OCS has not been identified.

12 Pulp and Paper Making/Chlorine Bleaching:

CGLI has contacted representatives of the pulp and paper industry regarding the suggested release of OCS [and Hexachlorobenzene (HCB)] from pulp and paper making processes. OCS

and HCB have **not** been detected in mill wastestreams. In addition, there is no evidence to support the contention that mills release OCS or HCB.

Details are provided in a February 1992 report prepared by the Water Resources Branch of the Ontario Ministry of the Environment[8] and in the discussion which follows in the section of this report entitled "Critical Review of the Battelle Report."

The OME letter explains that the only indication of OCS or HCB release was contained in a single report from the Ontario Ministry of Energy and Environment, which reported MISA monitoring data. Upon investigation, NCASI learned that "the preliminary data upon which the estimates are based were rejected from the MISA database after QA/QC review found sufficient irregularity in them to make it very doubtful that the mills were actually emitting the compounds."

In addition, NCASI consulted with pulp and paper chemistry specialist Dr. Douglas Reeve of the University of Toronto. Dr. Reeve examined the chemical reactants and conditions necessary to produce OCS and HCB and compared them with pulp and paper making process conditions. He concluded that pulp and paper making processes "have never favored formation of highly chlorinated substances. The use of high or complete substitution of elemental chlorine with chlorine dioxide reduces the tendency even further." OCS and HCB are, of course, very highly chlorinated materials. All U.S. mills will soon be converted to complete chlorine dioxide substitution in compliance with EPA's new CLUSTER rule for this sector. This process is also commonly used at Canadian mills. Conditions have not favored the formation OCS and HCB in pulp mills. The recent and continuing conversion to the complete substitution process moves process conditions even further away from the likelihood that these compounds would be formed.

PCDD/F releases in pulp mill discharges have been an issue in the past. Mr. Larry LaFleur, a National Council of the Paper Industry Air and Stream Improvement (NCASI) Fellow, has reviewed the mechanisms necessary for OCS formation in the "Critical Review of the Battelle Report" section of this report. His review of the chemistry involved in bleaching processes, the mechanisms necessary for OCS formation, and extensive EPA sampling and monitoring efforts in a variety of bleaching processes where evidence of occurrence of potential OCS mechanisms would have been evident, have shown that there is "no justification for extrapolating from the historical presence of PCDD/F in pulp bleaching to the potential for this process to produce OCS."[9]

13 Chlorinated Solvent Production:

The Halogenated Solvent Industry Alliance (HSIA) reports that:

> Chlorinated solvents production does appear to have been a source of OCS contamination in the past. The available data cited in the draft report indicate that OCS can be produced

8 Report on the Analysis of the Quality Assurance and Quality Control Data for the MISA Pulp and Paper Sector, Water Resources Branch, Ontario Ministry of the Environment, February 1992, PIBS 1846, Log 91-2310-038.

9 See the discussion starting on page 37 of this report.

during the manufacture of chlorinated solvents and that OCS has been detected in the effluent from solvent manufacturing operations in studies conducted in the 1980s or earlier. The draft report does not attempt, however, to evaluate changes in the manufacturing process over the last 10 to 15 years. As a result, the report bases its conclusions about potential releases from solvents manufacture on practices that are no longer applicable. Today, waste products from solvent production are either reused in other processes, incinerated, or placed in secure landfills. According to information provided by EPA's Office of Pollution Prevention and Toxic Substances, moreover, OCS is largely dependent on the process used to produce the solvent.

Rather than use current data on OCS in solvent production effluent or, even, data that were collected in the 1970s or 1980s, the draft report bases its estimate for OCS on estimates of HCB releases from solvent production. This approach is significantly flawed for two reasons. The draft report provides no rationale to support its assumption that the ratio of OCS to HCB in releases of solvent production will be the same as the ratio found in sediment. The April 1998 estimates for HCB releases used in the draft, moreover, are greatly exaggerated.

Appendix A of the draft report provides a table of OCS/HCB ratios found in sediments that have been reported in the literature. A review of this table suggests that the ratio varies considerably, even among samples taken in the same area at the same time. It is reasonable to suspect, based on the information, that there may be processes that differentially alter the concentration of one pollutant relative to the other. Pereira et al (1988), in fact, suggest a "salting-out" effect in the Bayou d'Inde area to explain differences in levels found in sediments and water. Despite the variation in the reported ratios, the draft report offers no rationale for using the ratio found in sediment or for selecting the average of all of the reported ratio information.

Although HSIA does not necessarily disagree with the use of an OCS/HCB ratio for estimating potential releases, we believe that the ratio should be based on actual measurements from waste streams. HISA notes that pollutant information is available from samples of waste streams from production facilities in Ontario and Louisiana.

Use of the OCS/HCB ratio also depends, of course, on the accuracy of the estimate for HCB. HSIA has submitted comments to EPA's Air Office concerning the flaws in the April 1998 inventory for HCB, the source used by the draft report. To summarize our comments, EPA's inventory analysis uses Toxic Release Inventory (TRI) reporting data from a small number of facilities and extrapolates these data to all U.S. facilities based on production capacity rather than actual production.

HSIA believes that TRI data overestimate actual emissions because they are based on theoretical (worst-case) calculations, rather than actual measurements. In reviewing the TRI data for 1996, however, we find a total of 451 pounds of HCB reportedly released to the environment (250 pounds to water, 201 pounds to air) from manufacturers of chlorinated solvents. We suggest that this is a more accurate estimate to use as a basis for

estimating OCS releases than the figure reported in EPA's April 1998 inventory.

Based on the above discussion the estimated OCS release rate reported by the Battelle report is at least 2000 times too high. The actual release rate, especially that to the Great Lakes Basin, is not thought to be significant.

14 Coke Production:

Test results from Stelco Inc.'s Lake Erie Steel Company failed to detect OCS in coke oven emissions. Environment Canada has determined that the iron and steel sector is not a source of OCS. An error that occurred in 1990 reporting activities suggested otherwise.

The "no source" conclusion is based on the fact that the Ontario government tested integrated steel plant effluents in 1989 and 1990 for various pollutants including OCS as part of its Municipal/Industrial Strategy for Abatement (MISA). OCS was not detected at any facility including Stelco Inc.'s Lake Erie Steel Company, which produces over 600,000 tons of coke annually. The effluent tested measured less than 0.0026 ug/l OCS (i.e. below detection limit). The RMDL was 0.010 ug/l.

15 Waste sites:

The second Battelle report discusses potential OCS releases from closed or active landfills. EPA's Vicki Thomas has said that these area sources would be dealt with as other aspects of the Binational Toxics Strategy. This direction and the fact that these potential sources are part of ongoing RCRA regulation and remediation programs precludes the consideration of confirmed, unconfirmed, or suspected OCS releases from waste sites as an industry source. This sector discussion should be removed from the Battelle report.

16 Tire Manufacturing:

OCS release from the tire manufacturing sector is suggested by the Battelle report based on reports that natural rubber contains HCB. Industry contacts explain that this assertion comes from an April '98 report from EPA, based on analysis of tire tread compound which industry has determined to have been in error. In addition to spurious results relating to HCB, the presence of carbon disulfide and toluene were also reported to EPA. These, too, have not been found in industry follow-up tests. The quantity of HCB reported to EPA was small, leading to the proposal of an AP-42 emission factor of 9.29×10^{-9}. Because the factor is so small, industry has not vigorously attempted to correct this error. However, if this insignificant quantity is to be pursued in light of BNTS challenge goals, the record must be corrected. Additionally, EPA has historically reported the presence of chlorine in natural rubber. This may lead to speculation regarding a potential for the formation of chlorinated compounds in rubber products. The industry has found no evidence that natural rubber contains chlorine. Contacts report that there is no data which directly links rubber products, or raw materials, to OCS.

Other Sources:

CGLI continues to seek information regarding suggested OCS releases in the following sectors.

- **Chlorinated Solvent Incineration**
- **PCB Incineration - Waste Oil Burning**
- **Rare Metals Production**

Information received from these contacts will be relayed to Environment Canada and U.S. EPA at a later date.

The Status and Trends of OCS in the Environment

17

To confirm the lack of significance of the potential or suggested OCS sources which may remain in the Great Lakes Basin, a review of the status of OCS levels in the environment has been made by Dr. Daniel W. Smith of Conestoga Rovers Consulting. The following analyses reviews his findings regarding the current status and spatial and temporal trends of octachlorostyrene (OCS) in Great Lakes media. These questions were addressed:

- What are current concentrations of OCS in Great Lakes media?
- How have concentrations changed over time?
- How do concentrations vary from place to place?
- What can be deduced concerning current sources and future trends?

Methods: Data on OCS concentrations in Great Lakes media were collected from available sources. Emphasis was placed on analyses of data sets that were extensive and relatively consistent in terms of methods of collection and chemical analyses. While some of the data have been published, most recent data were sought and obtained from various agencies. The Canadian Wildlife Services (CWS) supplied more recent data from that agencies long range monitoring of colonial bird eggs. The Ontario MOE supplied recent data on OCS concentrations spottail shiners from the Niagara River. Unpublished data from MOE's monitoring of water and suspended solids in the St. Clair and Niagara Rivers were obtained from MOE. The USEPA supplied unpublished data on OCS concentrations in Lake Ontario, collected by the EPA.

Temporal trends were analyzed based on the model of first order decline

$$C_t = C_0 * \exp^{(rt)}$$

Where C_t is the concentration at time t, C_0 is the concentration time 0 or the start, and r is the first-order rate constant. First-order decline assumes that proportional rates of decline are constant over time, that is

$$\frac{dC}{C\,dt} = \text{constant}$$

First order decline is the most appropriate model for decline of persistent chemicals in the environment because the fate processes that reduce ambient concentrations (e.g., burial, biodegradation, volatilization, photolysis, and dilution) are themselves first order processes. Because temporal trends are assumed to follow first order kinetics, temporal trends were tested with linear regression analysis after transforming concentrations to the natural logs. This produces the following equation

$$\text{Ln}\,(C_t) = \text{Ln}\,(C_0) + r * t$$

In which all parameters are the same as in the first equation. The existence of a first order decline

can then be tested, statistically, with linear regression of log concentration on time of collection. Logarithmic transformation of concentration also tended to normalize residuals, a requisite for the use of parametric statistics.

Because absolute changes in concentrations fall as concentrations fall, first order reactions will always trace a concave up path when plotted on the usual linear XY graph (Figure 1). The inevitable concave up shape, unfortunately, misleads many viewers into believing that concentrations of organochlorines (OCs) are stabilizing over time. Thus, all temporal trends will be depicted on the semilog scale. Time is plotted on the linear X-axis while untransformed concentrations are plotted on a logarithmic Y-axis (Figure 2). Readers unfamiliar with the semilog scale should be advised of the following. First, equal distances on the logarithmic Y-axis represent equal percentage changes in concentration. Consequently first order declines now trace a straight line (Figure 2), eliminating the optical illusion of stabilization that occurs on the linear XY plot. Secondly, absolute changes in concentration tend to look smaller than when plotted on the linear Y-axis, as shown in Figures 1 and 2. When assessing progress over time, therefore, it is important for the reader to look closely at the Y-axis.

Because percent declines per year are more accessible than first-order rate constants, rates of decline over time will be described in the text below in terms of percent declines as opposed to the first order rate constants produced by the regression analyses.

Results

Gull Eggs from the Great Lakes

The CWS eggs sampling program is the best available data base for determining status and trends of organochlorines in the Great Lakes. Since the early 1970s, CWS has assessed OC concentrations in gull eggs from a number of colonies across the Great Lakes. The positions of the colonies are depicted in Figure 3. The gull egg data are extensive over time and space and have benefited from a relatively consistent sampling and analytical methodology (described in Bishop et al. 1992 and Petit et al. 1994)10. Another advantage of the gull egg data is that the data are regularly disseminated and available to the Great Lakes research community. Thus, the strengths and limitations of these data are better understood than other Great Lakes data sets (e.g., see Smith 1995a, Hebert et al. 1996, Hebert et al. 1998).

These data were statistically analyzed (by colony and by Great Lake grouping) to determine whether trends were statistically significant. OCS in herring gull eggs declined significantly ($p < 0.05$) from 1987 to 1998 in eggs from all colonies except three – Leslie Spit (Toronto Harbor) and Snake Island on Lake Ontario, and Chantry Island on Lake Huron (Figure 4). In the latter three cases, the regressions were marginally significant (e.g., $p < 0.10$). Moreover, when the data from all colonies on a Great Lake were grouped together, rates of decline are highly significant for each Great Lake.

10 For complete reference citations see bibliography in Appendix V.

On average, OCS concentrations in gull eggs from colonies on Lakes Erie, Huron, and Ontario tended to be higher than those from Michigan and Superior (Figure 5), although there was considerable variability between colonies on the same Great Lake (Figure 6). OCS concentrations were only sometimes elevated in gull eggs taken from colonies near historical sources such as Channel Shelter Island on Saginaw Bay, the Fighting Island Colony on the Detroit River, and the colonies on Lake Ontario. On the other hand, OCS concentration from the Port Colborne colony on the eastern Basin of Lake Erie and the Niagara River colony were both quite low despite their proximity to historical sources in the Ashtabula and Niagara Rivers (Battelle 1998). The rates of OCS decline over time among lakes were remarkably consistent, despite intra-lake variability. By colony, rates of decline varied from about 9% per year at Channel Shelter Island to about 24% per year at Double Island (Figure 4), both on Lake Huron. However, the rates of decline were not significantly different (ANCOVA, $p > 0.05$) across all Great Lakes colonies, and all colonies tended to decline at an average rate of 18% per year. Concentrations of OCS in most colonies are approaching the detection limit (about 1 ppb) (Figures 5 and 6). Eggs were below the limit of detection at least once between 1995 and 1996 in all colonies except two – the Middle Island colony in Lake Erie and the Channel Shelter Island colony in Lake Huron.

Conclusion: From 1987 to 1998, concentrations of OCS in gull eggs fell significantly and somewhat rapidly, on average about 18% per year (Table 3). The rates of decline did not differ statistically among colonies, and declines were very uniform across lakes and connecting channels. These decreases have reduced the concentrations of many colonies to levels near the limit of detection. Spatially, colonies from Lakes Ontario, Erie, and Huron have similar concentrations. Concentrations of OCS in gull eggs from colonies on Lake Superior and Michigan are similar to each other but lower than from the other Lakes.

Spottail Shiners from the Niagara River and Lake Ontario.

Another very useful long-term database for OC in the Great Lakes is provided by spottail shiners represent These data are the property of the OMOE and the Canadian Government, and collection and analytical methods are described in Suns et al. (1982, 1993) and Suns and Hitchin (1992). As with the gull-egg data, the spottail-shiner data benefit from relatively consistent methods over the long term as well as frequent sampling over time and space. However, only the data from the Niagara River were obtainable for this report. OCS concentrations in spottail shiners from the upper Niagara River are only rarely above the detection limit, making temporal trends analyses impossible. However, OCS concentrations in shiners from the lower Niagara River were generally above the limit of detection in the beginning of the sampling period in the mid-1980. When less than detect values are assigned the value of ½ the detection limit, OCS concentrations in the lower Niagara River are estimated to have fallen about 8% per year ($p < 0.05$, Figure 7)11.

11 Because OCS data are limited and often below the limit of detection, values, usually 1/2 the detection limit, were assigned to concentrations that were below the limit of detection. This practice allowed use of the information contained in analyses that were below the detection limit and seemed a reasonable compromise between the two possible extremes of applying the detection limit or zero. The latter is also problematic because zero cannot be log-normalized.

Use of 1/2 the detection limit is only recommended for use with trends analyses and does not imply, nor should it be

Conclusions: Concentrations in shiners taken from the lower Niagara declined at about 8% per year, falling from about 4 ug/kg in the mid 1980s to less than detection in the mid 1990's.

Lake Trout from Lake Ontario

The Canadian Department of Fisheries and Oceans (F&O) collects lake trout and smelt from each of the Great Lakes on an annual basis. F&O data are not readily available to the public or Great Lakes scientific community, so the quality, methods, and extent of these data could not be ascertained. According to information presented in Huestis et al. (1996), lake trout samples from Lake Ontario are analyzed for OCS. These data show significant ($P < 0.05$) declines, about 10% per year, in OCS over time in Lake Ontario lake trout.

Conclusion. Concentrations of OCS fell significantly, about 10% per year, in Lake Ontario lake trout from 1977 to 1993.

Water and Suspended Sediments from the Niagara River

The Upstream/Downstream monitoring group samples water at the beginning and end of the Niagara River, at Fort Erie and Niagara-on-the-Lake. These data, therefore, provide information on water quality conditions in Lake Erie, the Niagara River, as well as information about loading of OCS to Lake Ontario. This is a high quality database with relatively consistent methods over time and very frequent sampling. These data are also regularly published and easily obtainable by the Great Lakes science community.

OCS data were obtained from the Upstream/Downstream sampling group for the period between 1989 and 1995. During this period, water samples were generally taken every week. Whole water samples were divided into aqueous and suspended sediments, and chemical analyses were conducted on these two fractions. Although there are MDLs reported for both fractions -- 0.05 ng/l for the aqueous fraction and 2.7 ng/g of suspended sediment -- concentrations well below the MDL (20% or less of the MDL) are routinely reported. Thus, these reports produce three types of data: estimated concentrations above the MDL, estimated concentrations below the MDL, and data listed as below the detection limit.

At Fort Erie, at the origin of the Niagara River, 281 aqueous fractions and 285 sediment fractions were analyses[12]. None had a reportable concentration of OCS. Thus, OCS was never detected in 566 analyses representing about 285 water samples. OCS was detected at the mouth of the Niagara River at Niagara-on-the-Lake. For the aqueous fraction, 270 analyses were conducted.

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inferred to mean, that the actual concentrations are really 1/2 the detection limit. The practice should not be used as an indication of substance presence or for purposes of source identification. In many cases (e.g., with suspended sediment concentrations in the Niagara River and with bottom sediments), actual concentrations are probably considerably less than 1/2 the detection limit.

12 The number of aqueous data points does not equal the number of suspended sediment data point because data for one or the other medium are sometimes, albeit infrequently, rejected because of QA problems.

Concentrations for the aqueous fraction were 43 times between 1989 and 1991, but not since then. For the adsorbed fraction, reportable concentrations of OCS were detected more frequently concentrations, about 55% of the time. To determine long-term trends, total water concentration of OCS for each sample was estimated in the following manner

[OCS]total water = [OCS]aqueous + [OCS]adsorbed * [suspended solids].

Given the large number of analyses below detection, the results of a trends analysis will depend somewhat upon what values are given to unreported values. To insure that trends were real, various values were given to the unreported values for adsorbed OCS: 1/2 the detection limit (1.35 ng/g), 1.0 ng/g, and 0.37 ng/g, the lowest value reported. OCS was rarely reported in the aqueous fraction, so unreported data in the aqueous fraction were set equal to zero.

No matter how non-reported values were treated, OCS concentrations were estimated to have fallen significantly over the period. However, the estimated rate of decrease was dependent upon what values were used for unreported values. OCS concentrations declined by about 40% per year when unreported values were set equal to 0.37 ng/l, but only about 28% per year when unreported values were set equal to 1.35 ng/g, one half the detection limit (Figure 8). Ignoring the aqueous fraction and setting unreported values equal to 1.35 ng/g, OCS concentrations on suspended sediments fell about 21% per year. These analyses demonstrate that OCS concentrations really did decline over this period. However, detecting future declines will become more difficult as more and more analyses yield non detect values.

All of these measured rates of decline are probably faster than the long-term average. Oliver and Charlton (1988) measured OCS in the Niagara River several times in the fall of 1982. They found an average OCS concentration of 0.06 ng/l in whole water, which is approximately three times the geometric mean concentrations found in 1989. These two dates trace a 15% per year decline. Similarly, OCS concentrations in the Niagara Bar (discussed below) demonstrate long-term declines of about 14.5% per year.

Conclusion. From 1987 to 1995, OCS concentrations at Fort Erie were always lower than the detection limit in both water and suspended sediments. At Niagara-on-the-Lake at the mouth of the Niagara River, OCS was detected at reportable concentrations on a semi-regular basis, especially adsorbed to suspended sediments. OCS concentrations in whole water and suspended sediments fell rapidly over this period, between 21% to 40% per year, depending upon the value applied to unreported values. Based on these data, loading of OCS to Lake Ontario is estimated to have decreased about 70% or more between 1989 and 1995.

Suspended sediments and water from the St. Clair River

MOE monitors water at two points in the St. Clair River, Port Edward at the beginning of the of the St. Clair River and downstream at Port Lambton. The methods are similar to those used in the Upstream/Downstream sampling: sampling on a frequent basis (every two to three weeks), fractionation into an aqueous and sediment fraction, detection limits of 0.05 ng/l and 2.7 ng/g, respectively, and analysts who routinely report concentrations below the detection limit. Of 103

analyses of the aqueous fraction sampled at Port Edward between 1987 and 1996, only 5 samples had reportable concentrations of OCS. These 5 samples averaged 0.02 ng/l OCS. Only two of 111 analyses of suspended sediments had reportable concentrations of OCS.

Reportable concentrations were more frequent downstream at Port Lambton. Of 141 analyses of the aqueous fraction taken between 1987 and 1994, only 7 had reportable concentrations of OCS. However, OCS was regularly reported adsorbed to particles. About 90% of analyses of suspended sediment yielded reportable concentrations of OCS (Figure 9). When unreported concentrations are set equal to one half the detection limit, these data produce a significant decline of about 15% per year.

Conclusions: OCS concentrations have generally not been detected at Port Edward at the origin of the St. Clair River. Downstream at Port Lambton, OCS concentrations dissolved in water are also infrequently detected above the detection limit. However, concentrations adsorbed to suspended sediments are generally at reportable concentrations, although these concentrations appear to be falling at about 15% per year over the last decade.

Data for the St. Lawrence River/Outflow from Lake Ontario

Environment Canada also samples OCS at the origin of the St. Lawrence River. These data are diagnostic of St. Lawrence conditions as well as Lake Ontario. The data are apparently generated using the same general methods as with Niagara River and St. Clair River sampling. Reported detection limits were 0.07 ng/l for water and 2.7 ng/g for the adsorbed fraction. For 85 samples taken from 1989 to 1994, OCS concentrations were reported once in the water column and 11 times in the suspended sediment fraction. All of the reported concentrations were below the detection limits. The eleven concentrations reported for the sediment fraction averaged 0.9 ng/g. The single value reported for the aqueous fraction was 0.01 ng/l, which is $1/7^{th}$ the MDL13.

Conclusion. Concentrations of OCS in the headwaters of the St. Lawrence River/outflow of Lake Ontario are infrequently detected at concentrations that can be estimated. Current concentrations are well below the detection limit.

Bottom Sediments from Lake Ontario

Two sediment core samples have been taken from Lake Ontario and analyzed for OCS. Durham and Oliver (1983) took a sediment core in the Niagara Bar in 1981, and core samples from the Niagara Bar were taken in 1995 by New York Department of Environmental Conservation (NYDEC 1996). The two cores showed a consistent pattern (Figure 9). In both cores, OCS concentrations in sediments apparently peaked about 1960 and then declined at about 13.5%.per year (Figure 10). For the NYDEC sample, OCS concentrations in sediments deposited after about 1981 were always below the detection limit, which ranged from about 13 to 6.4 ug/kg.

13 As these data are below the MDL, they represent samples for which OCS is probably present extremely low levels, but the exact magnitude is unknown.

The yearly declines estimated between 1960 and 1981, when OCS concentrations were above the detection limit, can be extrapolated to the present. Assuming that past rates of decline continued to the present, OCS concentrations in Niagara Bay sediments in the early 1990s should be between 0.5 and 1.0 ug/kg (Figure 8). This projection can be compared to the sediment trap data from the Niagara Bar (Oliver and Charlton 1988) and suspended sediment data from the Upstream Downstream Monitoring of the Niagara River (see section above on the Water Concentrations in the Niagara River). Sediments captured in sediment traps should reflect sediments being laid down during that period. Similarly, OCS concentrations in sediments deposited in the Niagara Bar should be a function of OCS concentrations on suspended sediments at the mouth of the Niagara River, which is the source of most particles settling onto the Niagara Bar.

In both cases, however, concentrations of settling and suspended sediment must be normalized to organic carbon levels similar to those found in bottom sediments to reflect the reduced binding capacity of coarser, less organic sediments that finally settle onto the Niagara Bar. Most recently deposited Niagara Bar sediments are about 3.1% organic carbon (NYDEC 1996). Organic carbon concentrations found in sediment traps were about twice those found in settled sediments (Oliver and Charlton 1988). Thus, sediment trap concentrations were divided by two to normalize for organic carbon (Figure 10). The concentrations measured by Oliver and Charlton fall very near the extrapolation line.

The fraction of organic carbon in Niagara River suspended sediments varies considerably, ranging between about 5% to over 30% organic carbon (Kuntz 1988)14. Assuming a geometric mean concentration of 10% would require a correction factor of 3.2 to normalize the suspended sediment to the 3.1% organic carbon of the sediments deposited in the Niagara Bar. When concentrations of OCS on suspended sediments from the mouth of the Niagara River are divided by this correction factor, most recent suspended sediment concentrations also fit right on the extrapolation line (Figure 10). This combination of information suggests that OCS loading to Lake Ontario has continued to fall at about the same rate (about 14.5% per year) from 1960 to the present.

Conclusion: As evidenced by OCS concentrations in Niagara Bar sediments, loading of OCS to Lake Ontario apparently peaked in the early 1960s, and has fallen about 14.5 % per year since that time to the early 1980s, after which concentrations became too low to be detected. More recent data on settling particles in the Niagara Bar region and suspended sediments in the Niagara River have concentrations similar to those extrapolated from the long-term trends, suggesting that this rate of decline has continued to the present.

Additional Data on Status and Trends. OCS was measured in Lake Ontario water column twice, in 1984 (Oliver and Niimi 1988) and 1996 (EPA, unpublished data). Both samples were taken during spring overturn in open water areas of the Lake and were replicated at several sampling locations. Oliver and Niimi report a mean OCS concentration of 4.7 pg/l in the aqueous phase. For the 1996 EPA sampling, all samples yielded concentrations below the detection limit:

14 These data were kindly supplied by J. Merriman, Ecosystem Health Division of the MOE.

roughly 0.5 pg/l in the aqueous phase and 0.2 pg/l in the adsorbed phase. As OCS was not detected in any of the 4 samples (three stations with one station duplicated), it can be assumed that the real OCS concentration was well below the detection limit. Assuming that the concentration was ½ the detection limits, or about 0.25 pg/l. Using these two dates only, there was about a 95% decrease in water column concentrations of OCS, or about 22% per year. This observation should be treated with caution. Only two periods were sampled, and the analyses were conducted by different analysts.

Discussion.

The above analysis was limited to straightforward description of observable status and trends of OCS in Great Lakes media. These analyses addressed basic questions of how OCS concentrations have varied in time and space. In the context of the "virtual elimination strategy", there is also the less straightforward question of what spatial and temporal trends really mean. Specifically, can spatial and temporal trends in measured concentrations be used as an indicator of underlying trends in external loading?

The simple answer to this question is "no." The problem with inferring changes in loading from changes in ambient concentrations is twofold. First, measured concentrations in many media are often not good indicators of in-lake inventories, especially when measurements are limited. Second, for systems at non-steady-state with external loading, trends of in-lake inventories may be based largely upon internal fate processes and have little or nothing to do with trends in external loading (Endicott et al. 1992a,b, Smith, under review.) With respect to the first problem, concentrations of organochlorines in biota (lake trout, gull eggs, spottail shiners) are known to respond to a number of other factors in addition to abiotic concentrations and levels of external loading. These factors, which confound interpretation of observed trends, include winter weather, prey availability, aquatic prey chain length and structure, terrestrial vs. aquatic foraging, limnological factors, and potential effects of inter-lake migration (Rasmussen et al. 1990, Rowan and Rassmussen 1992; Smith 1995a,b, under review; Hebert et al. 1995; 1998) Concentrations of chemicals in the water column and sediments are confounded by sampling error and actual variability due to storms and mixing events as well as long-term changes in lake trophy and suspended sediments concentrations.

In view of the confounding factors affecting organochlorine concentrations, caution should be exercised when extrapolating observed trends, over time and space, in any of the media above to underlying trends in in-lake inventories, and from there, to trends in external loading. This is especially true of inferences based on small data sets and short time trends. For example, consider the OCS data for gull eggs from Lake Ontario (Figure 11). The long-term trend from 1987 to 1998, which shows a significant decrease in OCS concentrations over time, actually consists of three short-term trends: concentrations tended to remain constant from 1987 to 1993, fell precipitously, about 90%, from 1993 to 1995, and then rebounded somewhat from 1995 to 1998 (Figure 11).

Several factors suggest that none of these short-term trends is responding to underlying changes of in-lake inventories levels or external loading of OCS. For example, the initial period of stable

concentration is more likely attributable to one of the confounding factors affecting organochlorine concentrations in gull eggs (e.g., food chain effects and/or the weather effect). This is apparent because most of the organochlorines also show stable concentrations from the period 1987 to 1993 (Smith 1995a). The organochlorines have disparate sources of external loading to Lake Ontario, and it is not reasonable to expect that the loading of the different external sources of different organochlorines would be synchronized. The short-term pattern of stable OCS concentrations in gull eggs is also inconsistent with data from Niagara River loading. The Niagara River should be the primary external source of OCS to Lake Ontario. Loading of OCS from the Niagara River declined rapidly, from 70% to 80% at the same time that gull egg concentrations remained constant (Figure 8 vs. Figure 11). With respect to the precipitous decline of OCS concentrations from 1993 to 1995, it is highly unlikely for OCS inventories in Lake Ontario to fall much more than 10% per year, even under condition of complete zero loading (e.g., see Endicott et al. 1992a).

On the other hand, more reliable indicators of trends in ecosystem inventories, but not necessarily external loading, can be obtained by focussing on long-term trends and by looking for similar trends among different media. Despite potential problems with any one data set, there is a high degree of certainty that OCS concentrations have really been falling over the period from 1980 to at least the mid-1990s in Lake Ontario. As summarized in Table 3, there are statistically significant and quantitatively substantial declines in all of the following media:

inflowing Niagara River water concentrations (1989 to 1994)
spottail shiners residing in that inflowing water
in-lake water column concentrations (1994 to 1996, two dates only)
gull eggs (1987 to 1998)
lake trout (1977-1993)
in-lake sediments (1960 to 1981 or 1994 if suspended sediment data can be included).

Similarly, we can be reasonably certain that OCS concentrations in the St. Clair River/Detroit River are also actually declining, because OCS concentrations are declining in the water column and in gull eggs. Data on temporal trends in other Great Lakes areas are mostly limited to gull eggs. This might be problematic, except that OCS levels are falling at all of these other colonies, suggesting that OCS inventories are indeed declining in the Great Lakes. Equally important, Lake Ontario and the St. Clair/Detroit River are two of the three areas in which OCS levels are elevated. With the exception of Saginaw Bay, where OCS is also elevated in gull eggs, temporal trends in other Great Lakes areas are of less importance because levels in most media are already near or at the detection limit.

Keeping in mind the limitations of the data, the following addresses the questions posed at the beginning of this discussion.

- **What are current levels of OCS in Great Lakes media?**

As shown in Table 3, current levels of OCS in most media are now at the limit of detection or rapidly approaching this limit at most sites in the Great Lakes. The notable exceptions to this are

OCS concentrations in lake trout in Lake Ontario. Extrapolating past rates of decline (about 10% per year) onto early 1990's concentrations (about 30 ug/kg in whole raw lake trout) suggest that whole raw lake trout will continue to exceed the current detection limit (1ppb) till about 2025. It is also likely that OCS is above the detection limit in fish from the other Great Lakes, and potentially the St. Clair/Detroit River and Niagara River. Assuming a relatively constant relationship between gull eggs and fish, it is likely that OCS would be about as high in Lake Erie and Lake Huron fish as in Lake Ontario. OCS might also be detectable in very large lake trout from Lake Superior and Lake Michigan.

- **How have levels changed over time?**

In all media with adequate data, levels of OCS are decreasing significantly and, compared to other organochlorines, relatively rapidly, e.g., 8% to 30% per year (Table 3). Rates of decrease over time are generally highly statistically significant, quantitatively substantial, and consistent across media, time, and space. It can be concluded with a high degree of certainty that OCS concentrations in the Great Lakes have declined dramatically over the last two decades.

- **How do concentrations vary over space, i.e., from place to place?**

Gull egg data suggest that OCS burdens in Lake Huron, Lake Erie, and Lake Ontario are higher than in Lakes Superior and Michigan, although there is substantial intra-lake variability between colonies from Lake Erie and Huron. Elevated concentrations appear to be related to historical sources in Saginaw Bay, the St. Clair River, and Lake Ontario. Data from other media are limited, but tend to support the spatial trends found in gull eggs.

- **What can be deduced concerning current sources and future trends?**

The available data suggest that atmospheric sources were probably never an important source of OCS to Great Lakes ecosystems. Gull eggs colonies with elevated concentrations are generally downstream of historical sources of OCS in Saginaw Bay, the St. Clair River, and the Niagara River. Concentrations of OCS in gull eggs from colonies on Lake Michigan and Lake Superior, which are far away from historical sources, tend to be about 3 to 4 times lower than those downstream of suspected historical sources. It is also important to note that concentrations of OCS in gull eggs from all of the colonies are falling at about the same rate in all Lake groupings (Figure 5). This observation is inconsistent with the hypothesis of significant current atmospheric inputs, as one would expect atmospheric dependent sites to decline at a different rate than colonies primarily affected by past and current riverine and point sources. The rapid decreases in OCS concentration in gull eggs and the other media also suggest that current atmospheric loading is relatively insignificant and allows unimpeded declines of OCS in the lakes. Consistent with all of these observations, OCS is rarely if ever detected in air monitoring near the Great Lakes (Dann 1997).

If atmospheric loading of OCS can be assumed to be negligible, that leaves current external loading from point and non-point sources and internal loading from sediment inventories due to past external loading. It is critical to differentiate between internal and external loading. External

sources are generally controllable and likely to yield some benefits if controlled. Sediment inventories, on the other hand, are not readily easily controlled and yield less certain benefits as they will remediate naturally, albeit slowly, without further action.

The two different sources should produce different patterns over time and space. Systems whose OCS concentrations are tightly controlled by external sources should have very site specific and unique temporal patterns, because external source control will be a site-specific function of regulatory commitment, local economic conditions, amenability to control, and other site specific factors. Thus, if, as is often hypothesized, sites on the Niagara River are a major current source of OCS to the Lake Ontario, one would expect declines in OCS in the Niagara River and Lake Ontario media to be episodic and tied tightly to specific remediation activity. It is also expected that the temporal patterns of decline will be very different from OCS declines at other sites, and very different from declines of other chemicals (e.g. PCBs and DDE) not associated with sources of OCS.

The patterns of decline for systems controlled by internal sediment stores are likely to be very different from those controlled by current external sources. As the fate processes controlling declines in sediments are relatively constant across time and space and across PTS chemicals, one would expect systems controlled by internal inventories to decline at fairly similar rates through time, across lakes, and among persistent toxic chemicals. The data, while limited, seem more consistent with the latter hypothesis. The very similar declines of OCS in the gull eggs across colonies suggests some common mechanism of decline (potentially, for example, fate processes affecting sediment inventories.)

Great Lakes system dominated by internal sediment inventories should also have orderly declines of different persistent toxic substance. That is, concentrations of different organochlorines should decline in a predictable fashion based on the vulnerability to fate processes affecting concentrations in the sediments. More volatile and degradable chemicals like hexachlorobenzene should dissipate faster from the Great Lakes than more stable, less volatile chemicals such as Mirex and dieldrin. PCBs are of intermediate vulnerability to various fate processes and should dissipate with an intermediate speed. The predicted rates of relative decline for internal inventories of various organochlorine can be estimated from the model of Endicott et al. (1992a) under a condition in which external loading was reduced to zero. In this case, long-term declines of these chemicals depends on vulnerability to various loss processes. These estimated zero-loading declines can be compared to yearly declines observed for lake trout in Lake Ontario (Huestis et al. 1986). As can be seen from Figure 12, there is a significant relationship between predicted and observed declines of different organochlorines in Lake Ontario lake trout (regression analysis, $p < 0.05$). That is, as predicted, the different organochlorine are declining in a significantly orderly process based on their vulnerability to internal fate processes. This significant relationship further supports the hypothesis that external loading is unimportant. It is also important to note that OCS is actually declining faster than predicted. At the least, this graph demonstrates that OCS, which has received little regulatory attention in the last several decades, is declining considerably faster than compounds like DDT, PCBs, and TCDD, which have received much regulatory attention and have been under very strict regulation. This observation is inconsistent with a system dominated by external sources, which ought to be more controllable

than internal sediment inventories.

There are other data to substantiate that current concentrations of OCS in Lake Ontario are based on internal sediment inventories as opposed to current external loading. Loading from the Niagara River can be estimated from the Upstream/Downstream monitoring. Best estimates of early 1990s loading from the Niagara River are about 4.3 to 6 grams per day, depending upon what values are assigned to non-detection data. According to Endicott et al, model, this loading of OCS should produce lake trout concentrations of about 5.2 to 3.8 ug/kg in whole lake trout. These predicted values are 6 to 8 times lower than observed concentrations for this period, about 31 ug/kg (Huestis et al. 1996). The discrepancy between observed and predicted concentrations also supports the hypothesis that OCS concentrations in Lake Ontario are largely due to internal sediment inventories, as opposed to current external loading.

Table 3. Summary of results. Decreases are based on regression analyses. ND means not detected. NA means not applicable; some data sets had insufficient frequency of detected concentrations to permit trends analyses.

Medium	**Location**	**Time Frame**	**Decrease (% per year)**	**Most recent conc.**
Gull egg	Lake Ontario	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Erie	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Huron	1987-1998	Yes (16%)	Some ND
Gull egg	Lake Superior	1987-1998	Yes (17%)	Some ND
Gull egg	Lake Michigan	1987-1998	Yes (20%)	Some ND
Gull egg	Niagara River	1987-1998	Yes (17%)	Some ND
Gull egg	Detroit River	1987-1998	Yes (20%)	Some ND
Spottail Shiner	Lower Niagara River	1985 -1995	Yes (8%)	100% ND
Lake Trout	Lake Ontario	1977-1993	Yes (10%)	0 % ND
Water	Niagara River	1989-1995	Yes (16%-21%)	50% ND
Water	Upper Niagara River	1989-1994	NA	100% ND
Water	Lake Ontario	1984, 1996	Yes (20%)	100% ND
Water	St. Clair River (Port Edward)	1989-1996	Yes (15%)	>95% ND
Water	St. Clair River (Port Lambton)	1989-1995	NA	10% ND
Water	St. Lawrence	1989-1996	NA	90% ND
Bottom Sediments	Lake Ontario	1960-1981 (95)	Yes (12%)	100% ND

A Critical Review of the Battelle Report

18

OCS Formation Considerations

Mr. Larry LaFleur, a National Council of the Paper Industry for Air and Stream Improvement Fellow, has studied the mechanism of formation of chlorinated phenolic compounds, especially PCDD/Fs, extensively. He has reviewed the second Battelle report and has concluded that from a mechanistic and sound scientific process standpoint, the document is seriously flawed. His observations include the following.

I. Introduction

A fundamental premise of modern synthetic chemistry is that one needs to understand the basic reaction mechanism before one can reliably predict products. Even if one knows the proper mechanism, the appropriate reaction conditions (e.g., temperature, catalyst, sufficient time, proper solvents, suitable concentrations, etc.) must be present in order for the reaction to proceed. Many reactions which occur in one solvent, such as free radical chlorination in aprotic solvents, would be suppressed in a protic solvent such as water. Finally, the necessary starting materials must not only be present, but must be present in proportions conducive to the reaction. In many respects, synthetic chemistry is the science of successfully optimizing the various combinations of these variables to achieve a specific, desired outcome.

Accordingly, any technically creditable extrapolation from known sources of octachlorostyrene (OCS) to potential other sources requires a careful consideration of reaction mechanisms, conditions, and stoichiometry. Thus, sufficient evidence that each of these criteria have been met must be demonstrated before one would have sufficient cause to further examine a hypothesized new source.

In Sections II, III, and IV, we discuss mechanistic considerations, reaction conditions, and stoichiometry of some known sources of OCS. In this discussion, we highlight the types of corroborating data that would be necessary to extrapolate known OCS sources to other sources. In Section V, we give several examples of how a more critical consideration of these fundamental principles would show that there are no data to support the hypothesis that these processes are potential sources of OCS. In Section VI, we briefly discuss the Battelle approach to estimating an OCS inventory based on the EPA dioxin inventory and show that the underlying assumptions are fundamentally flawed.

II. Mechanistic Considerations

A. Hexachlorobenzene, octachlorostyrene, and PCDD/F

The Battelle report notes an apparent relationship between hexachlorobenzene and octachlorostyrene where PCDD/F have also been reported. These different mechanisms seem to arise where the starting materials and/or conditions are such that hexachlorobenzene can be

formed. Apparently, under these same conditions hexachlorobenzene can further react to form octachlorostyrene or it can proceed through a different series of reactions to form PCDD/F. Under these circumstances, there is an apparent relationship between octachlorostyrene and PCDD/F. However, it would be inappropriate to conclude that the reverse would also be true. If PCDD/F are formed by some other mechanism under other conditions, it may or may not coincidentally produce either hexachlorobenzene or octachlorostyrene. As is discussed in Section V, there are several examples of PCDD/F formation where there is no reason to suspect formation of octachlorostyrene.

B. The *de novo* synthesis hypothesis

In the review of sources commissioned by EPA in 1985, Schulman and Klingele15 discussed theoretical mechanisms for octachlorostyrene formation. They proposed the following hypothesis:

> "Each reaction in the stepwise formation of PCSs could fall into one of two broad categories:
>
> 1. ultratrace concentrations of reactants combine in high yield; or
>
> 2. high concentrations of reactants combine in ultratrace yields
>
> In the former case, the free energy of formation of the product at each step is lower than the free energies of reactants and other competing products. In the latter case, the free energies of formation of reactants and other products are lower than the PCS precursor products, but the statistics of the reaction chemistry assure that some of each of the successive precursor products will be generated in some amounts.
>
> Reaction conditions favoring the former case would probably involve high energy environments where polychlorinated aromatics like PCSs would be stable relative to other molecular configurations. Such conditions would be likely to prevail in high energy electro-, pyro-, photo- and thermochemical reaction environments. Reaction conditions favoring the latter case would involve lower energy reactions in which polychlorinated organic substances are reactants or intended products. Further, if PCSs were removed from the reaction environment fastest than other, more stable products, say via physical processes such as sorption to the walls or bottom of a reactor vessel or to particulate matter in the reaction matrix, significant quantities of PCSs could still be generated, even though not thermochemically favored."

Schulman and Klingele (1985) went on to propose a theoretical mechanism that might lead to the formation of octachlorostyrene through a series of high energy free radical chlorinations and polychloro alkyene radical coupling reactions. This mechanism is termed the *de novo* synthesis mechanism. This mechanism was not proposed based on any experimental investigations on their part, but was instead based on their review of potentially relevant published literature and their interpretations.

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15 For complete description of references see bibliography contained in Appendix VII.

Their final conclusions based on their deliberations were:

> "Whenever a carbon source is exposed to chlorine and large energy flux, as either electricity or heat, and indicator compounds such as carbon tetrachloride, perchloroethylene, and perchlorobenzene are produced, PCS is a suspected byproduct. Whenever aromatic compounds, particularly chlorinated ones, are exposed to conditions where chloroalkyl radicals may be present, PCS is a suspected byproduct."

We would add to those observations the fact that the chemistries used to support their hypothesis were free radical reactions occurring under extremely high energy conditions, and were often conducted with a very large excess of chlorine (relative to the available carbon). We believe these are important distinctions.

The Battelle report cites this hypothesis, describes it generally, but does nothing to further advance it or support it with new information.

Based on the rationalizations used to advance this hypothesis, the *de novo* mechanism is clearly a high energy free radical chlorination and coupling mechanism. In order to invoke this mechanism for a potential new source of OCS, one should provide supporting data to justify the hypothesis. As discussed in the Schulman and Klingele report, one should provide evidence of other intermediates or by-products that support that a similar mechanism is operative. These may include carbon tetrachloride, various tri- and tetra- chloro ethanes and ethylenes, hexachlorobutadiene, di-, tri-, tetra-, penta-, and hexachloro- benzenes, etc. Since many of these are actual commercial products, it would be necessary that more than just a single intermediate be identified to support the like mechanism argument.

C. Magnesium and nickel refining

In one reference, the Battelle report states that there are indications of formation of both OCS and PCDD/F (Oheme et al. 1989) in magnesium and nickel refining. The authors also note that the processes result in the formation of hexachlorobenzene. Oheme et al. describe a unique PCDD/F fingerprint where the PCDF to PCDD ratio is 50:1. This would indicate that it is appropriate to suggest formation of OCS from a source if, and only if, the hexachlorobenzene was demonstrated to be present and the PCDF to PCDD ration was approximately 50:1. A more detailed examination of the PCDD/F fingerprint reported by Oheme et al. (1989) should be performed, and additional criteria should be considered (e.g., the 1,2,3,7,8-PeCDD to 2,3,7,8-TCDD ratio was 11:1). These criteria would provide a technical justification for assuming a like mechanism might be operative. At the same time, it should also be pointed out that the Oheme et al. work explicitly pointed out the vast differences between the Mg and Ni refining PCDD/F fingerprint and the fingerprint typically observed in incineration sources. This is explicit evidence that there is a completely different mechanism than the one responsible for the OCS from Mg and Ni refining that may be operative in incineration sources.

D. Other metal refining processes

Doring et al. (1992) describe the concurrent formation of OCS, HCB, pentachlorobenzene

(PeCB), decachlorobiphenyl (DCB), and PCDD/F from a copper smelting process. Doring et al. (1992) describe conditions necessary for the formation of these compounds as follows:

> "A chlorine source is present (sodium chloride) and the reductive conditions transform Cl^- to Cl·-radicals. These are then able to chlorinate the aromatics formed by radical processes from the carbon source (coal) at the high process temperature."

They later note:

> "The chlorination roasting process of the copper slag has some similarities with the production of waterfree magnesium chloride (reductive conditions at high temperature (>700°C), presence of carbon and Cl-radicals)."

Much like the fingerprint for the above described Mg process, there is a clear predominance of PCDFs, with the PCDF/PCDD ratio at about 10:1.

This illustrates the importance of corroborating mechanistic hypotheses with confirmatory data. Only when clearly analogous conditions are observed and similar fingerprints are demonstrated (e.g., PCDF/PCDD ratio of 10:1, presence of HCB, DCB, and PeCB) can one reasonably infer the formation of OCS.

E. Perchloro solvent manufacturing

In the work reported by Pereira et al. (1988), which the Battelle report cites as evidence of a link between OCS and HCB, the authors also report the presence of high levels of di-, tri-, tetra-, and penta-chlorobenzenes, as well as hexachloro-1,3-butadiene and octachloronaphthalene as by-products of chlorinated solvent manufacturing. Thus, before invoking an argument that the presence of HCB is an indication of potential OCS via the same mechanism, evidence of these other co-contaminants that would support the hypothesis of a like formation mechanism should be provided. Otherwise, there is no justification for supposing a like mechanism.

To summarize, before any surrogate chemicals like PCDD/F or HCB can be used as indications of the potential for OCS formation, there should be some corroborative data which provides supporting evidence that a like reaction mechanism is operative. Without such evidence, the extrapolation from one source to others using the presence of these proposed indicator compounds is technically insupportable.

F. Chlor-alkali production

The Battelle report sites the work of Kaminsky and Hites (1984) as evidence of the formation of OCS in the chlor-alkali process where carbon electrodes are utilized. In work published by Rappe et al. (1990), a PCDD/F fingerprint for this type of process was shown to produce a large predominance of PCDFs. For instance, sludge from electrodes was found to contain 52,000 pg/g 2,3,7,8-TCDF vs. non-detectable levels of 2,3,7,8-TCDD. Similar high ratios were found for the higher homologues. Thus, inferring a relationship between known sources of PCDD/F from electrolytic processes and the potential for production of OCS would only be technically defensible if it were demonstrated that the PCDFs clearly dominated the fingerprint. If another

fingerprint is observed, it would be sufficient evidence that an alternative mechanism is operative and that, in the absence of other evidence concerning that mechanism and its by-products, it would be inappropriate to infer the formation of OCS.

III. Reaction Conditions

Table 4 provides a partial summary of conditions where OCS has been demonstrated to form (as described in the Battelle report, not independently verified). All can be characterized as high energy processes. Some involve high electrical currents, some high temperatures, and some both. In many cases, Cl_2 gas or other chlorinated solvents are used to create certain atmospheres, and conditions are such that they are clearly intended to react. Characterization of other potential sources of OCS should include careful comparison of the conditions known to produce OCS and those of the candidate process.

Table 4. Reaction Conditions of Known Sources of Octachlorostyrene

Process	Temperature	Energy Input	Carbon Source	Chlorine Source
Chlor-alkali	not specified	electric current	carbon electrodes	brine and Cl_2 produced
Mg refining	1000-1200°C	electrodes	carbon electrodes	Cl_2 atmosphere
Al degassing	600°C	unspecified, (sufficient to melt Al metal)	hexachloro-ethane	hexachloro-ethane or Cl_2
Cu smelting	700°C	unspecified, (sufficient to melt Cu metal)	coal	8% NaCl under reducing conditions
Secondary Pb smelting	1260°C	incineration	battery casings	PVC separators

IV. Stoichiometry

Examination of the metals refining processes described in the Battelle report strongly indicates that in most cases there is excess chlorine relative to carbon (high chlorine to carbon ratio). This is also true for the production of carbon tetrachloride and tetrachloroethane. If one considers the chlor-alkali process, where a large volume of Cl_2 is produced from a comparatively small mass of carbon (in the form of the electrodes), there is also a high Cl/C ratio. Under these circumstances, it seems apparent that the potential for the formation of highly chlorinated compounds like OCS exists. However, it would not be appropriate to assume that if the right temperature and/or other conditions were present, the same potential for formation of OCS exists where the ratio is the opposite.

To a certain extent, dilution may also be an important consideration. Reactions that proceed in high yield at high concentrations may not proceed at all if performed under dilute conditions.

V. Examples of the Use of These Principles

A. Pulp bleaching

A perfect example of the need to provide some supportive evidence of like mechanisms is the insupportable extrapolation of the historical presence of PCDD/F in pulp mill effluents and the suggested formation of OCS. It has been well established that the formation of PCDD/F in pulp bleaching was caused by electrophilic aromatic substitution of the unchlorinated dibenzo-p-dioxin and dibenzofuran (Kringstad et al. 1988; Voss et al. 1988; Berry et al. 1989; LaFleur et al. 1990). This type of ionic chemistry occurs because bleaching is performed in an aqueous environment. Free radical chemistry (as invoked by the Schulman and Klingele *de novo* formation hypothesis) is detrimental to the quality of the pulp; thus, steps are taken to suppress this chemistry. In older bleaching processes, this involved the use of 12 to 15% chlorine dioxide, a free radical scavenger. The active chlorinating agent responsible for the formation of PCDD/F in pulp bleaching is Cl_2. In order to eliminate the potential formation of PCDD/F in bleaching, the US and Canadian pulp and paper industry has moved to the use of chlorine dioxide bleaching processes. The switch to this bleaching chemistry has virtually eliminated all TCDD/F formation, and forms the basis of the NPDES effluent guideline limitation recently promulgated by EPA.

EPA conducted extensive sampling and monitoring of a variety of bleaching processes in the development of their effluent guideline (Federal Register 1998; US EPA 1993). This work included testing for many of the compounds that would provide evidence for other potential OCS mechanisms. Included in these analyses were carbon tetrachloride; tri- and tetra-chloro ethanes and ethylenes; di-, tri-, and hexachlorobenzenes; hexachlorobutadiene; and even styrene itself. EPA found no evidence of the presence of these compounds in the bleach plants they studied. This provides further evidence that the types of high energy free radical chemistry required to form OCS are simply not present in pulp bleaching.

To summarize:

The historical formation of PCDD/F in the bleaching process has been demonstrated to be due to an electrophilic aromatic substitution mechanism, <u>not</u> a high energy free radical mechanism.

Since free radical chemistry has undesirable effects on pulp quality, steps are taken to minimize it.

The pulp industry has changed its bleaching practices to the point where TCDD/F formation is virtually eliminated. These process changes have significantly reduced the incidental formation of other chlorinated organics as well.

EPA's data generated during their development of the pulp and paper industry effluent guideline demonstrate the absence of other indicator compounds that should be present if the *de novo* OCS mechanism was operative.

Taken together, there is no justification for extrapolating from the historical presence of PCDD/F

in pulp bleaching to the potential for this process to produce OCS. In fact, the clear understanding of the reaction mechanisms responsible for the presence of PCDD/F in historical bleaching processes is evidence that OCS would not be expected.

B. Vapor phase degreasing

The Battelle report seems to liken the process of vapor phase degreasing with aluminum degassing. In the case of the aluminum degassing process, the temperatures are above the melting point of aluminum (reported by Battelle as 600°C), and either hexachloroethane or chlorine gas are introduced to force their reaction with hydrogen. Comparing this with solid metal parts at or just below the boiling point of the solvent (e.g., 74°C for 1,1,1-trichloroethane) and inferring a potential for the formation of OCS is not technically sound.

C. Pesticide manufacture

The Battelle report sites pesticide manufacturing as a potential source of OCS. The discussion seems to involve mostly 2,4-dichlorophenol and products made using it as an intermediate. The process cited in the Battelle report is the controlled chlorination of phenol using a reasonably selective chlorination agent. There is nothing in this process that even begins to suggest the kinds of conditions necessary to produce OCS.

The authors state, "The methods for producing 2,4-dichlorophenol include the direct chlorination of phenol and/or monochlorinated phenol using chlorine or sulfuryl chloride (SO_2Cl_2) with chlorination promoters and stabilizers. In as much as this reaction is known to form CDD/CDFs, it is by analogy, suspected of forming OCS," citing Kirk-Othmer 1996. We have examined the Third Edition of the reference (which is the only edition we had ready access to), and find that the statement that "In as much as this reaction is known to produce CDD/CDFs…" is a very misleading interpretation. Kirk-Othmer noted that polychlorophenols are starting materials for the synthesis of PCDDs and use 2,4,5-trichlorophenol as the starting material for 2,3,7,8-TCDD. There is no indication that chlorination is the mechanism responsible. For a discussion of the currently accepted mechanism for PCDD formation in chlorophenol manufacturing, see the following discussion on pentachlorophenol. Other workers (e.g., Firestone et al. 1972) have analyzed technical formulations of dichlorophenolics and found no dioxin contamination.

D. Pentachlorophenol (PCP) production

Generally, the incidental formation of PCDDs during pentachlorophenol manufacturing is thought to be due to the strong basic conditions and condensation of the chlorophenolate salts with each other (see US EPA 1980 for discussion of reaction mechanism). The initial condensation forms a polychlorodiphenyl ether, which then undergoes an intra-molecular reaction to form polychloro-p-dibenzodioxin. Since technical pentachlorophenol has significant levels of tetrachlorophenols, the PCDD distribution is predominated by OCDD, followed by varying amounts of HpCDD and HxCDD. Generally, PCDFs are at much lower levels. It is also notable that polychlorohydroxydiphenyl ethers are co-contaminants of PCP (Jensen and Renberg 1972; Jensen and Renberg 1973; Nilsson et al. 1974). This fingerprint or product distribution does not resemble any product distribution associated with known sources of OCS. There is no similarity

in the reactions responsible for PCDD formation in PCP manufacturing (which are largely ionic) and the *de novo* high energy free radical chlorination and coupling reaction described by Schulman and Klingele (1985). There is no indication that any of the other OCS precursors are present. Thus, no evidence has been presented or is available indicating that there is any similarity to the mechanism for PCDD formation in pentachlorophenol and any known mechanism for OCS formation.

19

VI. Estimating an OCS Inventory Based on the Presence of PCDD/F

The Battelle report outlines a series of assumptions around ratios of HCB, PCDD/F, and OCS to develop emission factors, then uses the Oheme et al. (1989) sediment data to develop a numerical ratio for extrapolating PCDD/F data to predict or inventory other OCS sources. As was discussed previously, the fingerprint from the metals refining process studied by Oheme et al. (1989) was specifically noted by the authors to be unique. This is actually data that indicate that one should not use this as the basis of a conversion factor for any source other than other metal refining processes, or perhaps the chlor-alkali process, since it clearly demonstrates that this source is unique. Until a link has been established between OCS and a given mechanism of PCDD/F formation, it is totally inappropriate and counterproductive to the goals of the Binational Toxics Strategy to generate "generic" PCDD/F-to-OCS emission factors to estimate source emissions or to develop an OCS inventory. Thus the entire rationale used in Section 4.2 to establish a cornerstone for developing an OCS source inventory is fatally flawed and should be discarded.

20

Fate Based OCS Release Rate Estimation

Mr. Robert Bailey has reviewed the premise put forth in the second Battelle report regarding the calculation of OCS/HCB/Dioxin ratios from sediments, and their application to suspected source generation rates. He has found this presentation to be seriously flawed. Estimates of OCS releases to the Great Lakes Basin have been grossly over estimated. His comments follow.

As the Battelle authors found when attempting to compile a report on sources of octachlorostyrene (OCS), there is essentially no direct information available on production and releases of OCS. Their approach was to summarize what information they found on the occurrence of OCS in the environment and potential sources. However, there was no segregation of the data by time so that the conclusions are based in large part on older information, reflecting technology and practices from the 1970s and earlier. In addition surrogates were incorrectly used to estimate OCS emissions and concentrations in the environment. **The conclusion that OCS may be currently, 1999, emitted in significant quantity in the Great Lakes region is not supported by the available data.** The reported dramatic decreases in most of the observed concentrations over the past 30 years and concurrent and continuing decreases in related chemicals suggest that OCS may be disappearing from sight in the Great Lakes.

Environmental Concentrations

In the Great Lakes and elsewhere the observation of OCS in the environment has been the clue to production and release of OCS from a variety of industrial processes. Sediment cores in Lake Ontario show a peak in the concentration of many chlorinated chemicals, chlorobenzenes, pesticides and OCS around 1960 (Kaminsky and Hites, 1984, Durham and Oliver, 1983)[16]. Since that time, waste disposal as well as production technology have improved with great reductions in the release of these chemicals to the environment. In fact, already by 1981 Durham and Oliver (1983) reported the concentration of OCS in Lake Ontario sediments had dropped by over 95% from its 1960 concentration. Huestis et al. (1996) report an approximately 90% decrease in the concentrations of both OCS and HCB in fish from Lake Ontario between 1977 and 1993. The concentration of OCS in Niagara River suspended sediments has continued to drop during the period of 1990 through 1995 (Niagara River TMP).

Sources of OCS

The major recent (post-1980) sources of OCS in the environment seem to have been landfills which received waste from the old processes (pre-1980) described in the Battelle report. For example, prior to the 1970s landfill in the Niagara Falls area received "taffy tar" containing OCS and many other chlorinated organics from the production of chlorine. However the release of OCS from these old landfills has been and will continue to be reduced by (a) cleaning old storm sewers of accumulated chemicals and (b) diverting the current landfill leachate from the landfills to wastewater treatment (Niagara River TMP). This storm sewer cleaning and landfill leachate diversion to wastewater treatment has been and is an ongoing part of the cleanup of the Niagara River.

A second example of reduced OCS emissions is the cleanup of the Ashtabula River. Emissions of OCS and other chlorinated chemicals into the Ashtabula River have been essentially eliminated and a dredging program is planned to remove contaminated sediments which could spread into Lake Erie (Mahan, 1999).

The formation of trace levels of OCS has been documented for a number of processes where chlorine and carbon are present at high temperatures or in electrochemical reactions (Vogelsang, 1986; Kaminsky and Hites, 1984). In general these processes have not been studied closely for OCS because of its low concentrations. As suggested by Schulman and Klingele, it is logical to attempt to predict OCS emissions from the HCB or PCDD/Fs emissions from a variety of processes. The formation of OCS along with HCB, hexachlorobutadiene and polychlorodioxins and furans (PCDD/Fs) from the successive accumulation of two-carbon units, as proposed by Schulman and Klingele, is easy to accept based on the pyrolysis experiments of Lahaniatis (1989). Similarly, the pyrolysis of hexachloroethane used in degassing of molten aluminum in laboratory experiments by Westberg et al. (1997) and qualitatively confirmed by Vogelsang (1986) is consistent with Schulman and Klingele's proposal. However, the formation of PCDD/Fs seems to

16 For complete description of references see bibliography contained in Appendix VIII

have a large surface catalysis component which varies widely under different conditions and may be different for OCS. The variations reported in the mixtures of PCDD/Fs from different processes also introduce a great deal of uncertainty in the ratio of OCS production to that of PCDD/Fs. (Summing the different congeners based on their toxicity to calculate a TEQ adds another layer of uncertainty). HCB is chemically more like OCS so that it may be a better surrogate for estimation of OCS concentrations in the environment. However, neither HCB nor TEQ can be considered a good surrogate for OCS in the absence of information linking OCS to each of the wide variety of processes considered in the Battelle report.

In addition, HCB is formed as a byproduct in some specific reactions in the production of highly chlorinated pesticides such as dimethyl tetrachloroterephthalate. Thus, the use of surrogates such as HCB, in the absence of specific information on emission ratios, must be used for only preliminary, order of magnitude, estimates of OCS emissions. Differences in the environmental degradation rates of OCS and surrogates could also change the observed ratio, especially in old samples, and not enough information is available at present to confidently assign the expected change in ratio.

Estimates of OCS emissions from HCB and PCDD/Fs were made in the Battelle report. However, this author will outline below several defects in the Battelle report's estimates of OCS emissions. The first error was taking the relative concentrations of OCS and HCB in sediments as reflecting their water concentrations without correcting for their different partition coefficients. Also, the Battelle report based its ratio of OCS to TEQ (PCDD/F) solely on data from a study of one river, the Elbe. This author proposes using an alternative study based on 400 sites in the U. S. (Kuehl and Butterworth, 1994).

The use of HCB concentrations in environmental samples as a measure of OCS needs to take into account their different physical properties which affect their partitioning in the environment. Neutral chemicals adsorb on sediments in proportion to their octanol/water partition coefficient, Kow (Karikoff et. al., 1979). The log Kow of OCS is estimated to be approximately 7.46 from structure activity correlations (SRC online Kow) and the log Kow of HCB, approximately 5.5 (Mackay et. al., 1992). Thus, OCS is estimated to adsorb about 100 times more strongly on sediments than HCB. That is, the concentration of OCS on sediment would be 100 times that of HCB at equal water concentrations.

The OCS/HCB sediment concentration ratio for some sediments are:

Durham and Oliver (1983)	0.15, mean, 1900-1981, Lake Ontario
Oliver and Bourbonniere (1985)	0.11, mean, 1980, 1982, Lakes Huron, Erie
Krieg and Krausch (1993)	0.15, mean, 1985-87, Elbe Estuary
Drouilliard et al. (1996)	0.26, mean, 1996, Detroit River

Thus, the concentration of OCS is estimated to be between 0.01 and 0.001 of that of HCB in the water. Presumably, the relative concentrations of OCS and HCB originally emitted would therefore also be between 0.01 and 0.001.

Atmospheric concentration measurements of OCS and HCB are likely to represent current emission ratios. However, such measurements have not been carried out extensively. Hoff et al. (1992) reported atmospheric measurements of OCS and HCB in 1988-89 in Canada near the shore of Lake Ontario. Unfortunately due to experimental design error, their sampling system did not collect all of the HCB during the summer but still the mean concentrations of HCB were nearly 100 times those of OCS, 54 vs. 0.71 pg/m^3. More recent measurements by Dan et al. (1999) did not detect OCS most of the time. HCB is included in the suite of compounds being regularly monitored in the International Atmospheric Deposition Network (IADN) program in the Great Lakes. Results from this program generally show a substantial and steady decline in atmospheric concentrations of HCB and other chlorinated chemicals since 1991 (Cortes et al., 1998, Hillery et al., 1997).

A factor for estimating the environmental concentration of OCS relative to that of 2,3,7,8-TCDD can be derived from the work of Kuehl and Butterworth (1996) in their survey of fish from nearly 400 sites throughout the United States. They report a mean concentration of 2,3,7,8-TCDD in fish of 13.6 pg/g, which made up 55% of the TEQ and a mean of 1.7 ng/g OCS. Converting the mean TCDD concentration to TEQ gives 25 pg/g TEQ which yields an OCS/TEQ ratio of 1700/25 or 68. Correcting for the increased bioaccumulation factor of OCS, $117x10^6$, vs. TCDD, $9x10^6$ (Battelle report) suggests a concentration factor of 68/(9/117) or OCS = 5.2 TEQ. Using this procedure, the concentration of OCS in the environment, and presumably emissions, would be five times the TEQ concentration. This factor can be compared with the OCS/TEQ factor of 653 used in the Battelle report which was derived from data in the Elbe River. The large number of non-detected OCS concentrations which were included at half the detection limit in the study by Kuehl and Butterworth lead to some uncertainty in the factor of five but this uncertainty is probably less than the overall uncertainty in using such a surrogate for OCS as TEQ.

Mr. LaFleur has shown that the one-size-fits-all approach used by Battelle to suggest OCS sources is flawed. Additionally, the errors discussed above in the procedure which were used to establish their ratio factors produce erroneous release rate figures. Going through Table 4 of the Battelle report applying a multiplier of 5 to the dioxin emissions and 0.01 to the HCB emissions yields a different perspective on OCS emissions, about 60 pounds OCS emissions per year for the entire U. S. versus the 4000 pounds estimated in the Battelle report. Dr. Smith's review of OCS levels in the environment have led him to the conclusion that air deposition is not a significant input vector for the Great Lakes. Given this finding, out-of-basin sources must be discounted from the 60 pound per year figure. Once the correct analytical data is used to determine if a source or sector actually releases OCS, the proper surrogate ratio is identified and applied, the "source" is only included if it is in the Great Lakes Basin, and the continuing operation of the "source" is confirmed, the actual Great Lakes Basin OCS release numbers will be substantially lower, and probably not significant.

These findings lead to the conclusion, that neither the current analyses for OCS in the environment or emission estimates based on surrogates support the Battelle report conclusion that there are significant emissions of OCS in the Great Lakes Basin.

OCS Pollution Abatement Technologies
(A pollution prevention approach)

As can be seen from the forgoing discussions, industries have used pollution prevention techniques to limit or eliminate OCS releases. In the case of the solvents industry, entire processes have been shut down. In other industries like the aluminum smelters, chemical substitutions have been made. The change from the graphite electrode process to metal electrodes in the chlor-alkali industry serves as an example of process technology changes which have resulted in the elimination of OCS sources. In other industries pollution control technologies have virtually eliminated OCS releases. Chemically assisted scrubbing equipment such as that employed by some aluminum smelters provide additional assurance that OCS and other compounds are not released in significant quantities. Utilization of these measures demonstrate that actions have been taken, over the past couple of decades, during a timeframe largely ignored by the second Battelle report which has provided for the virtual elimination of OCS releases from many industrial sources.

Findings and Conclusions

The following findings and conclusions can be drawn from the information provided above:

The Findings

This work has produced the following findings.

- In many industry sectors, pollution prevention measures have eliminated or significantly reduced OCS releases.
- In other sectors, Great Lakes Basin located processes which had previously released OCS have been shut down.
- In a few sectors, continuing OCS releases, if they actually occur at all, are at very low, often not detectable, levels.
- The examination of OCS environmental trend data shows that concentrations are decreasing rapidly. They are at or approaching detection limits in most media. If remaining OCS sources were significant, it would be expected that environmental concentration trends would be reaching a plateau, or in the worst case scenario, increasing.

The Conclusions

Based on the sector by sector analysis results and environmental trend data described in this report it is concluded that, for the sectors for which we have data, contemporary industrial sources of OCS in the Great Lakes ecosystem have been virtually eliminated[17].

17 The primary focus of this study has been the Great Lakes Basin. However, also included in this report is information pertaining to the likelihood of OCS releases at St. Lawrence River watershed based (Quebec) magnesium production and copper recycling (electronic equipment) facilities. Emissions potential at both was found to be unexpected or small.

This status has been achieved through exercise of pollution prevention and pollution control measures.

Appendix I
Octachlorostyrene Work Sheet

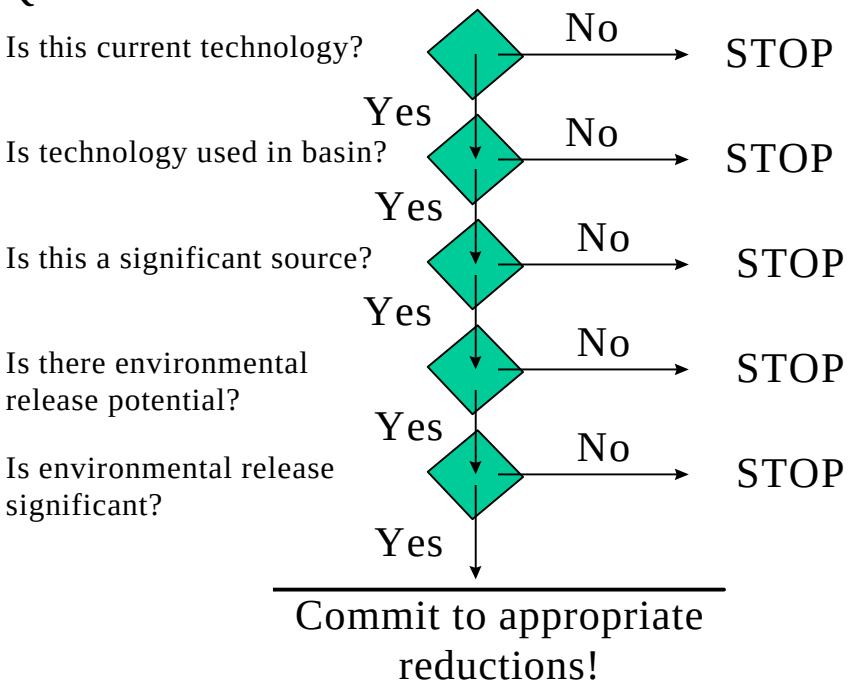
Potential Sources of OCS	Current Technology	Basin Technology	Source Significant	Environmental Release Potential	Significant Release Potential
Chlor-alkali production					
Graphitic electrodes	No	STOP			
Magnesium production					
Graphitic electrodes	Yes	No	STOP		
Raw material chlorination					
PVC Incineration					
Medical wastes					
Municipal wastes	Yes	Yes	No	Stop	
Chlorinated solvent incineration					
Cement kilns					
Haz. Waste incinerators	Yes	Yes	No	Stop	
Medical waste incinerators	Yes	Yes	No	Stop	
Municipal wastes incinerators	Yes	Yes	No	Stop	
Petroleum catalyst regen.					
PCB incineration					
Waste oil burning					
Auto fuel combustion	Yes	Yes	No	Stop	
Metal degreasing	Yes	Yes	N/A	No	STOP
Aluminum production					
Pri. - graphitic electrodes	Yes	Yes	No	STOP	
- degassing with Cl_2	Yes	Yes	No	STOP	
Sec. - Chlorinated coatings	No	STOP			
- demagging with Cl_2	Yes	Yes	No	STOP	

PVC coated wire recycling	Yes	Yes	No	Stop	
PVC polymerization/production	Yes	Yes	No	Stop	
Pesticides Manufacture					
Mono to tetrachlorophenol prod.	Yes	Yes	No	STOP	
Pentachlorophenol production					
Wood preservation	Yes	Yes	No	Stop	
Rare metals production					
Niobium extraction					
Tantalum extraction					
Pulp and Paper Making					
Chlorine bleaching	No	STOP			
Chlorinated solvent production					
High temp. chlorination	Yes	Yes	No	STOP	
Coke production	Yes	Yes	No	STOP	
Waste Sites					
Graphitic electrode disposal	N/A				
Electrolysis sludge disposal	N/A				
Incineration ash disposal	N/A				
Landfill fires	N/A				
Tire manufacturing	Yes	Yes	No	STOP	
dkp/3-8-98					

Appendix II

OCS Decision Tree

Questions:



Appendix III

Figures 1 - 12

Status and Trends of OCS In Great Lakes Media

Figure 1. First order decline (10% per year decrease) on linear XY plot

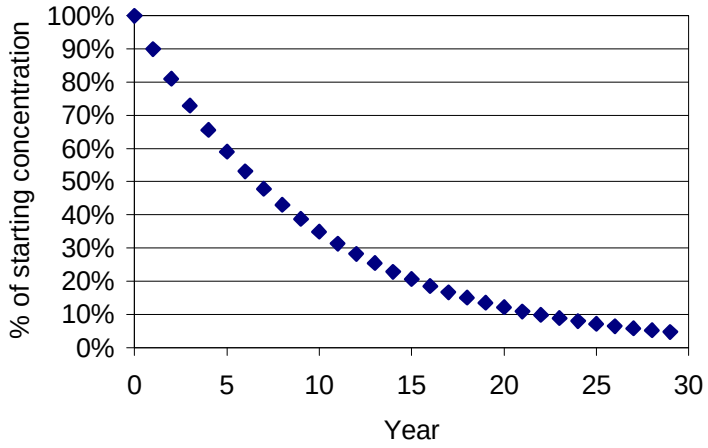


Figure 1. A first order decline graphed on the more usual linear XY plot.

Figure 2. First order decline (10% per year decrease) on semi-log XY plot

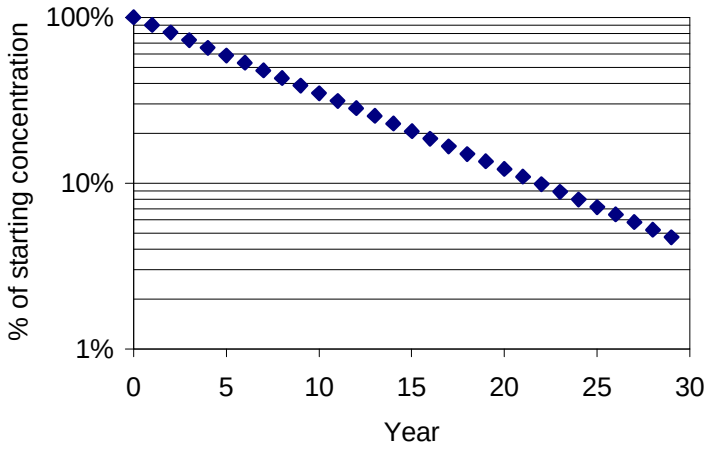


Figure 2. The same first order decline plotted on semi-log paper.

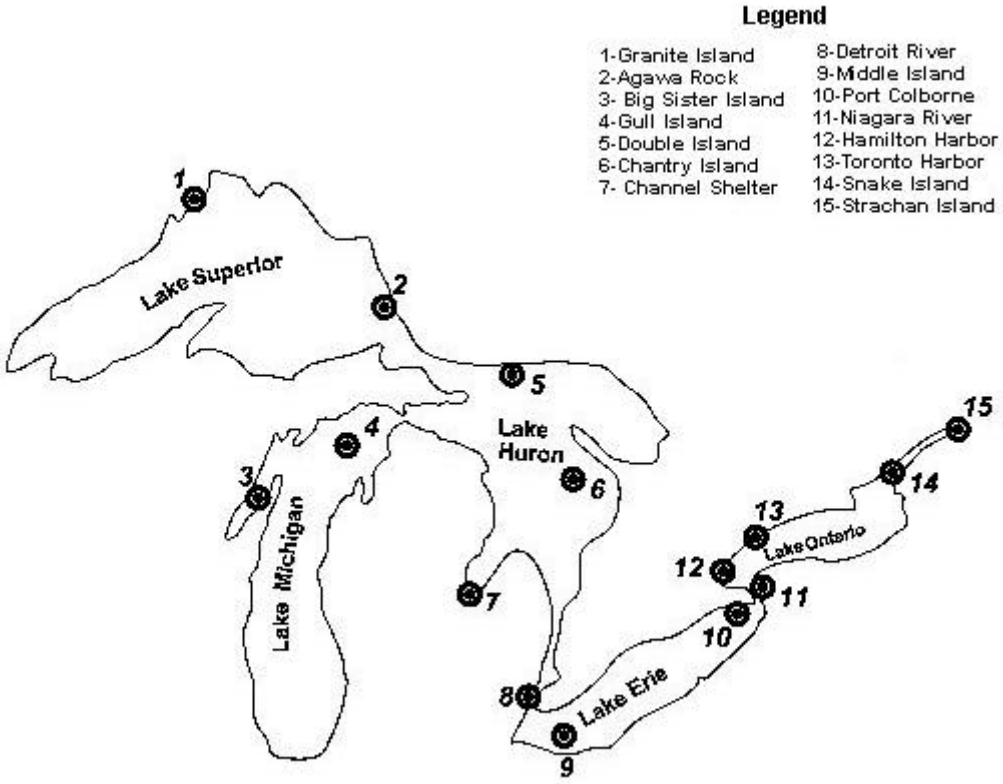


Figure 3. Location of Herring Gull colonies on the Great Lakes.

Figure 4. Yearly % Decline vs. Colony

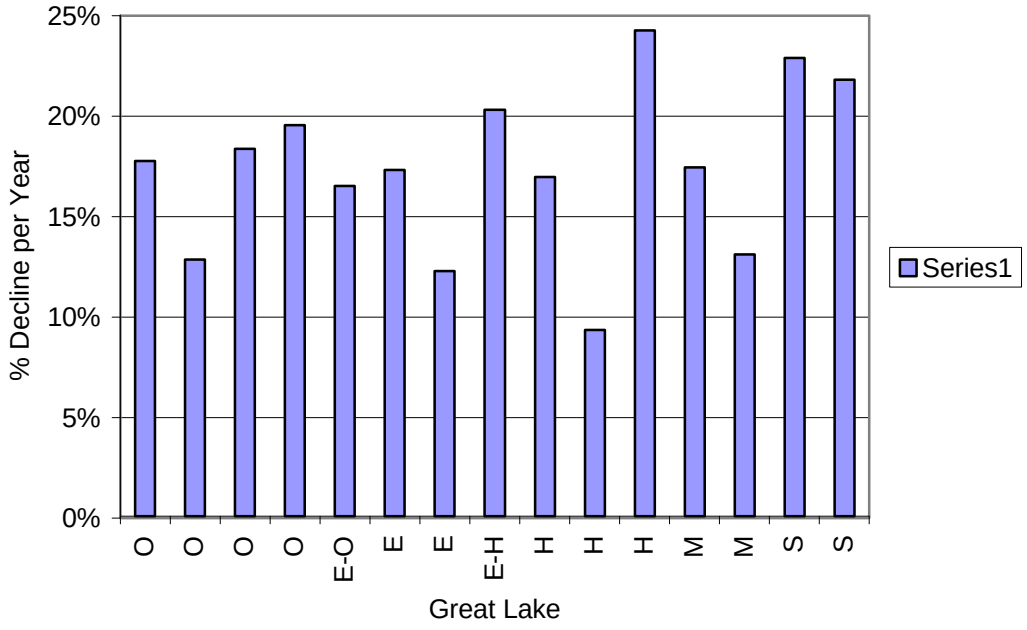


Figure 4. Best-fit % declines per year estimated from linear regression. Colonies are plotted in the following order which generally follow an east-west gradient: Lake Ontario colonies in the order of Strachan Island, Snake Island, Leslie Spit, Hamilton Harbor, Niagara River, Lake Erie colonies in the order of Port Colborne and Middle Island, Detroit River, Lake Huron colonies in the order of Channel Shelter Island, Chantry Island, and Double Island, Lake Michigan colonies with ?/ and ??, and Lake Superior colonies Agawa Rock and Granite Island.

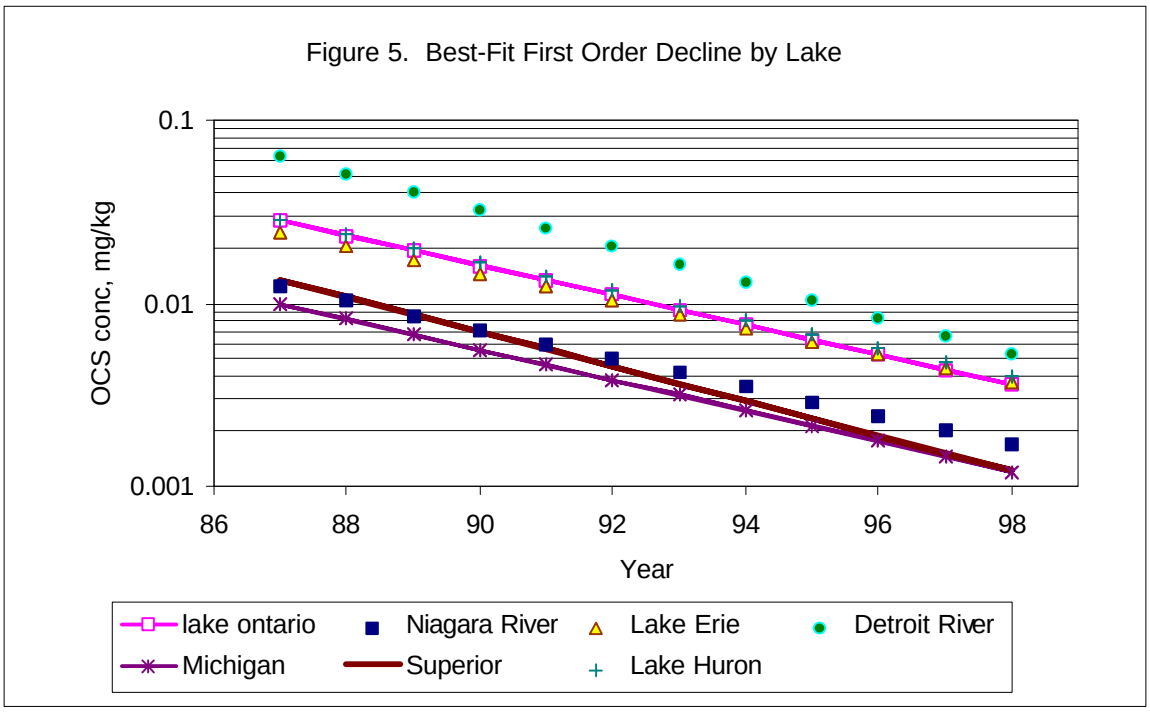


Figure 5. Best-fit declines of OCS in herring gull eggs grouped by Lake and Connecting Channel.

Figure 6. Mean OCS (94-98) versus Lake

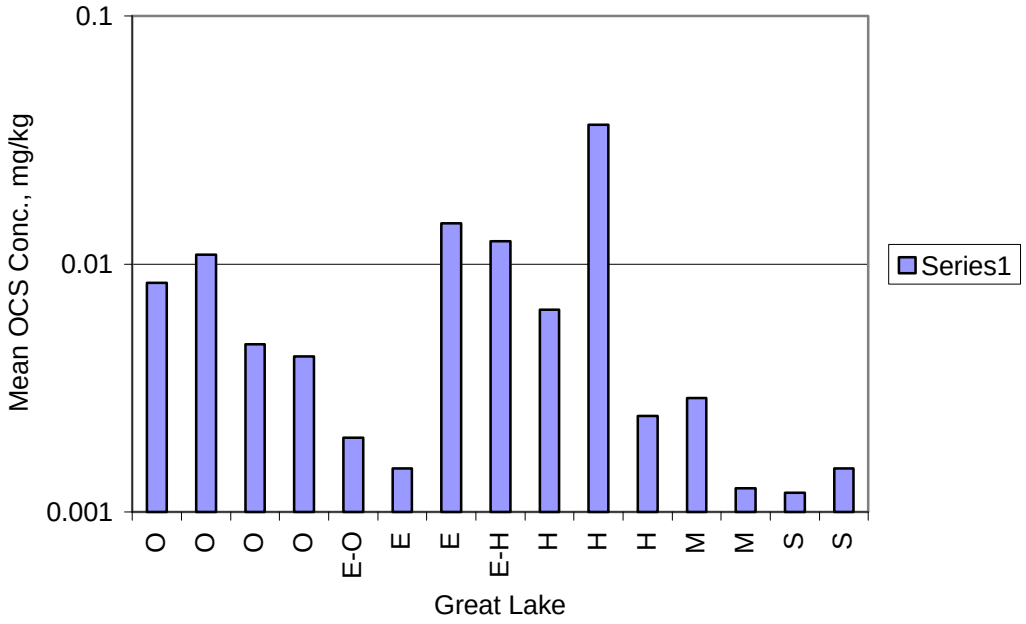


Figure 6. Most-recent (1994 to 1998) concentrations of OCS by colony. Sequence of colonies same as in Figure 6.

Figure 7. OCS in Spottail Shiners in Lower Niagara River (MOE Data)

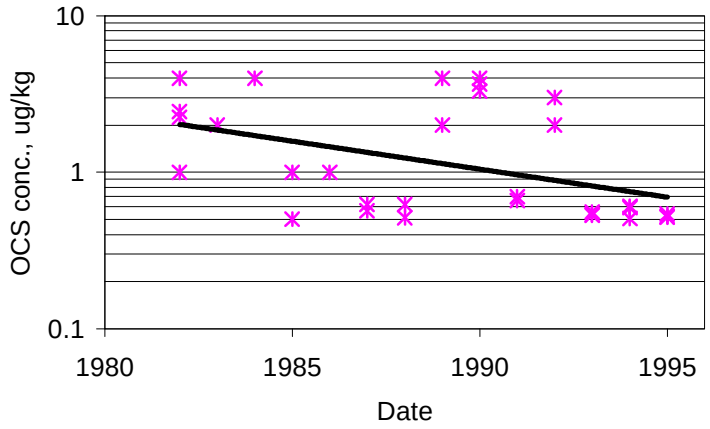


Figure 7. OCS concentrations in spottail shiners from the lower Niagara River. Values less than detection limit (1 ug/kg) set equal to 0.5 ug/kg. Some data points have been altered somewhat (e.g., 10% to 20%) to aid viewing when more than one sample on the same date had the same concentration.

Figure 8. Estimated whole water concentrations of OCS at Niagara-on-the-Lake

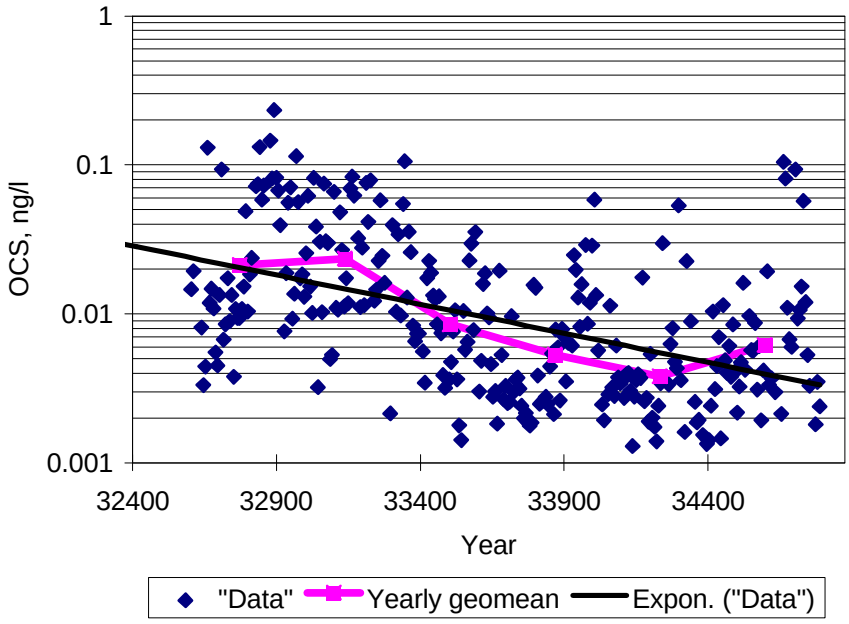


Figure 8. Concentrations of OCS in Niagara River water at the mouth of the Niagara River.

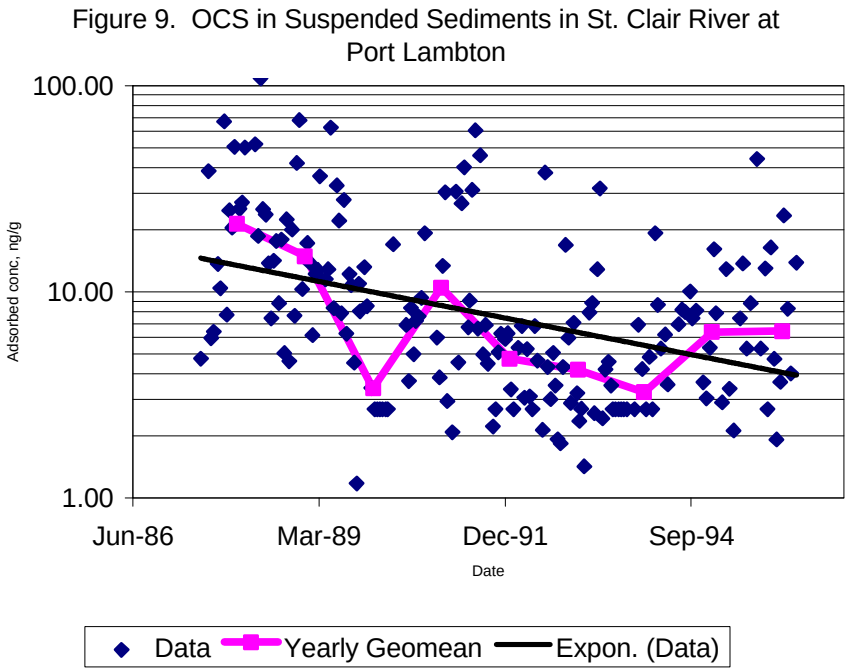


Figure 9. Concentrations of OCS on suspended particle from the St. Clair River at Port Lambton.

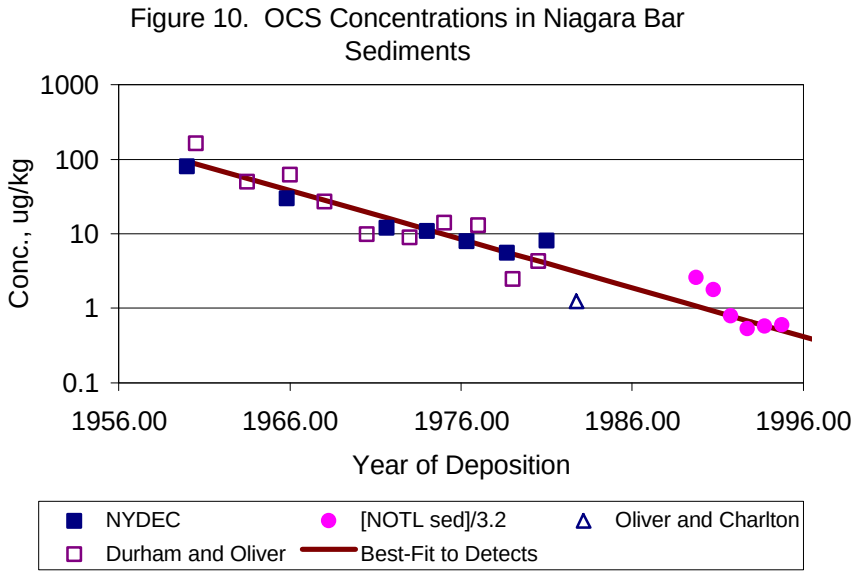


Figure 10. Concentrations of OCS in sediments from Lake Ontario. For the NYDEC sample, all analyses for sediments deposited between 1981 and 1995 were below the detection limit, but these data are not depicted on this graph.

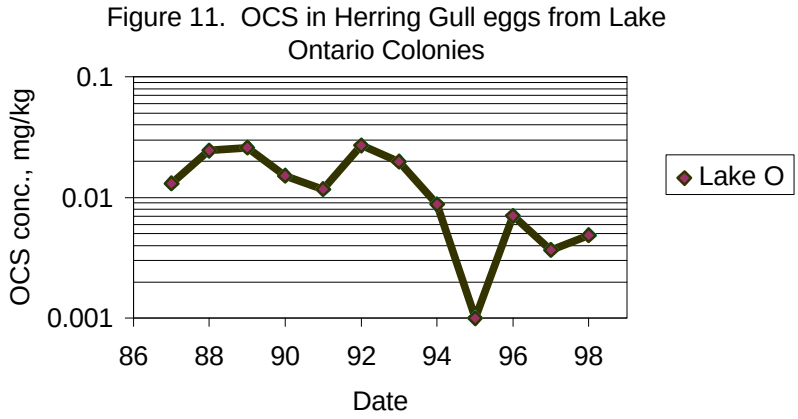


Figure 11. Mean concentrations of OCS in gull eggs from the four Lake Ontario gull egg colonies (Strachan Island, Snake Island, Leslie Spit, and Hamilton Harbor.)

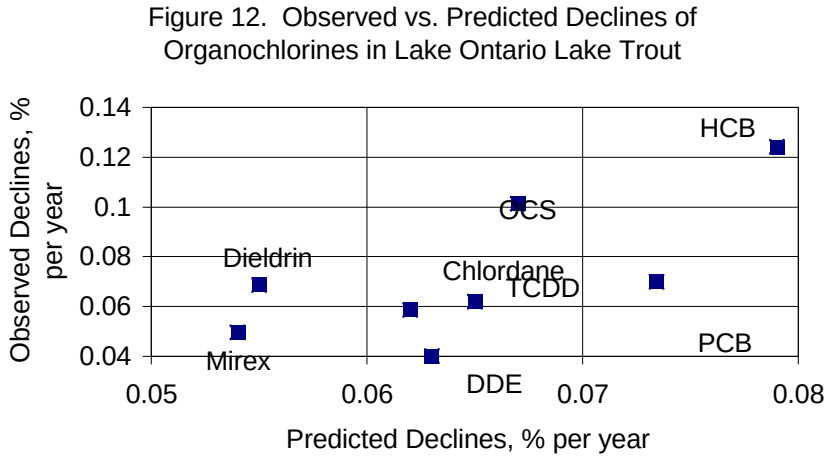


Figure 12. Observed versus predicted declines of different organochlorines in Lake Ontario lake trout. Predicted rates of decline (per year) from the Endicott et al. model (1992a) after cessation of loading. Observed rates are best-fit declines observed in lake trout, data from Huestis et al. (1996).

Appendix IV

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Status and Trends of OCS in Great Lakes Media
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March 1, 1999

Mr. Frank Anscombe
U.S. Environmental Protection Agency
Region 5 (G-17J)
77 West Jackson Boulevard
Chicago, IL 60604

Re: Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources, December 22, 1998 Draft

Dear Mr. Anscombe:

The Halogenated Solvents Industry Alliance, Inc. (HSIA) strongly disagrees witb the conclusions of the above referenced draft report concerning the potential contribution of chlorinated solvents production and metals degreasing to releases of octachlorostyrene (OCS). HSIA represents manufacturers of several chlorinated solvents, as well as numerous companies that use these solvents to degrease metal parts.

The draft report lists both metals degreasing and chlorinated solvents production as "documented" sources of OCS, and provides an estimate of OCS releases from solvents production. In the case of metals degreasing, the draft report provides no data to support its assertion that the degreasing process is similar to aluminum degassing. To develop its estimate of releases from chlorinated solvents production, the report employs old data, unsupported assumptions about the ratio between OCS and hexachlorobenzene (HCB), and flawed estimates of HCB emissions.

1 Metals Degreasing

Chlorinated solvents have for many years been used to degrease oils, greases, and other contaminants from metal parts. In the typical process, the solvent is heated to its boiling point and the contaminants are flushed by the solvent vapors as they condense on the part in the vapor zone. To ensure effective cleaning, contaminants are periodically removed from the boiling sump and disposed of as hazardous waste.

In its discussion of metals degreasing, the draft report suggests that:

> As in aluminum degassing, the reaction of chlorinated solvents with carbon deposits on the metal at elevated temperatures *may* generate OCS as a byproduct in the contaminated solvent drained from the machine or in the organic impurities that accumulate in the sump. *emphasis added*

The draft offers no data to support this contention, instead relying on the tenuous comparison to the aluminum degassing process. In the information provided for degassing, however, the draft notes that the production of OCS has been found to occur at 600° C. As indicated previously, the temperatures routinely encountered in the sump of a vapor degreasing are around the boiling point of the solvent (121°C or less). Clearly, the degreasing process does not provide sufficient energy to facilitate the series of reactions necessary to produce OCS. Even in a poorly maintained degreaser, where contaminated sludge has accumulated on the heating coils in the boiling sump and temperatures may rise above the boiling point, safety controls required on the equipment shut off the heat supply well below the temperatures encountered in aluminum degassing.

The report also fails to consider the fact that chlorinated solvent waste generated in the boiling sump of a vapor degreaser is subject to strict storage, handling, and disposal requirements under the nation's hazardous waste regulations. These wastes may not be discarded in a landfill and generally are destroyed in hazardous waste incinerators or cement kilns. To the extent that destruction of degreaser wastes may contribute to release of OCS, the draft report already addresses such wastes in its consideration of incineration processes.

2 Chlorinated Solvents Production

Chlorinated solvents production does appear to have been a source of OCS contamination in the past. The available data cited in the draft report indicate that OCS can be produced during the manufacture of chlorinated solvents and that OCS has been detected in the effluent from solvent manufacturing operations in studies conducted in the 1980s or earlier. The draft report does not attempt, however, to evaluate changes in the manufacturing process over the last 10 to 15 years. The most obvious change is that chlorinated solvents are no longer manufactured in the Great Lakes region. Secondly, as discussed in the enclosed information developed by EPA's Office of Pollution Prevention and Toxics (OPPT), the potential for OCS production is dependent on the process used to manufacture the solvents. Finally, in those facilities where OCS may be produced, waste products from solvent production currently are reused in other processes or incinerated, and are not discharged to surface wasters or disposed of in a way that could lead to such discharge.

3 Rather than use current data on OCS in solvent production effluent, or even data that were collected in the 1970s or 1980s, the draft report bases its OCS estimate on estimates of HCB releases from solvent production. This approach is significantly flawed for two reasons. The draft report uses the average ratio of OCS to HCB in sediments, without data or even a rationale to support the assumption that the sediment ratio would be the same as in solvent production wastes. The April 1998 estimate for HCB releases used in the draft, moreover, is significantly overstated.

Appendix A of the draft report provides a table of OCS/HCB ratios found in sediments that have been reported in the literature. A review of this table suggests that the ratio varies considerably, even among samples taken in the same area at the same time. It is reasonable to suspect, based on the information, that there may be processes that differentially alter the concentration of one pollutant relative to the other. Pereira et al (1988), in fact, suggest a "salting-out" effect in the Bayou d'Inde area to explain differences in levels found in sediments and water. Despite the variation in the reported ratios, the draft report offers no rationale for using the ratio found in sediment or for selecting an average of all of the reported sediment ratio information.

Although HSIA does not necessarily disagree with the use of an OCS/HCB ratio for estimating potential releases, we believe that the ratio should be based on

actual measurements from waste streams. We note that pollutant information is available from samples of waste streams from production facilities in Ontario and Louisiana. Data from the Ontario facility, collected in the 1980s, indicate an OCS/HCB ratio of 0 to 0.057 in effluent samples (King and Sherbin, 1986). The enclosed OPPT report, moreover, uses a ratio 0.073 in deriving its estimate of potential OCS production.

4 Use of the OCS/HCB ratio also depends, of course, on the accuracy of the estimate for HCB. HSIA has submitted comments (enclosed) to EPA's Air Office concerning the flaws in the April 1998 inventory for HCB, the source used by the draft report. To summarize our comments, EPA's inventory analysis uses Toxic Release Inventory (TRI) reporting data from a small number of facilities and extrapolates these data to all U.S. facilities based on production capacity rather than actual production.

HSIA believes that TRI data overestimate actual emissions because they are based on theoretical (worst-case) calculations, rather than actual measurements. In reviewing the TRI data for 1996, however, we find a total of 451 pounds of HCB reportedly released to the environment (250 pounds to water, 201 pounds to air) from manufacturers of chlorinated solvents. We suggest that this is a more accurate estimate to use as a basis for estimating OCS releases than the figure reported in EPA's April 1998 inventory.

Please do not hesitate to contact me if you have any questions about the information provided above.

Sincerely,

Stephen P. Risotto
Executive Director

Enclosures

APPENDIX G
OCTACHLOROSTYRENE

G.1 CHEMICAL PROFILE

Octachlorostyrene (OCS) (CAS 29082-74-4) is a polychlorinated styrene that is a possible byproduct of chlorine production, chlorination reactions, and metal product/finishing operations (EPA, 1998) such as the production of metallic magnesium (Knutzen and Oehme, 1989) and dry etching of aluminum (Raabe et al., 1993). OCS may also be formed by the high-temperature incineration of chlorinated hydrocarbons (EPA, 1998). OCS is not a commercial product, and no commercial uses are known. Industrial processes that may be sources of OCS include the following:

- Radical initiated chloralkene polymerization, a process involving aromatic radicals, vinyl or styrene monomers, and chlorine atom sources;
- Electrolysis of chloride salts in processes using graphite or carbon anodes at temperatures greater than 275°C. This process may be used in the production of chlorine, aluminum, sodium metal, tantalum metal, and niobium metal;
- Manufacture of metallic magnesium using carbon electrodes;
- Fused salt electrolysis, a process used to produce sodium from sodium chloride;
- Aluminum production that utilizes a smelting process created by Alcoa in 1976, that incorporates alumina, carbon, chlorine, and a carbon electrode at high temperatures;
- Incineration of chlorine-containing plastics and organic chemicals (EPA, 1984);
- Degassing of molten aluminum with hexachloroethane (HCE) (Westberg et al., 1997); and
- Production of perchloroethylene and carbon tetrachloride using the Stauffer or Scientific Design processes (Markovee and Magee, 1984).

Historically, OCS byproduct was generated in the manufacture of chlorine from aqueous sodium chloride or potassium chloride by an electrolytic process. The electrolytic process, involving an anode made of powdered graphite with a coal tar pitch binder, leads to the production of a mixture of chlorinated organics that are later removed as a waste byproduct. This waste byproduct, known as "taffy", may contain OCS. The improper disposal of the taffy may release OCS into the environment (Kiminsky, 1984). Powdered graphite anodes with coal tar pitch binders were used exclusively for chlorine production until 1979; however, the development of noble metal oxide coatings on titanium substrates has led to a drastic reduction in the use of graphite electrodes. Most chlorine producers presently use ruthenium oxide or titanium oxide coated titanium anodes rather than graphite anodes (Kroschwitz, 1994); five manufacturers are expected to still use graphite anodes in their production processes (EPA, 1986, EPA, 1995b). OCS production from operations not employing graphite anodes is considered unlikely due to the lack of a carbon source in these processes.

OCS has been identified as a byproduct from the manufacture of carbon tetrachloride (CTC) and perchloroethylene (PCE). These chemicals are commercially produced using the Stauffer or Scientific Design processes; both processes involve high-temperature chlorinolysis (550 to 600°C) of propylene in an excess of chlorine (Markovee and Magee, 1984). The recovered products of the reaction are CTC, PCE, and chlorine. Chlorinated, high-boiling residues are also produced; these residues form a "hex-waste" byproduct consisting primarily of hexachlorobenzene, hexachlorobutadiene, and hexachloroethene (HCE). Heavier compounds, including OCS, are present at lower concentrations (Markovee and Magee, 1984).

OCS is also a potential byproduct of the production of metallic magnesium. The process involves electrolyzing magnesium chloride to metallic magnesium and chlorine using a carbon electrode. The process leads to the formation of considerable amounts of chlorinated hydrocarbons, including OCS. According to the International Magnesium Association, there are two metallic magnesium plants operating in the United States that use carbon electrodes. The combined capacity of these two facilities is 100,000 metric tons of metallic magnesium per year (IMA, 1998).

OCS byproduct is also produced during degassing of molten aluminum with HCE (Westberg et al., 1997) at aluminum foundries and secondary smelting plants. Hydrogen gas from the surrounding water vapor is readily dissolved in molten aluminum and causes deficient mechanical properties in the resulting aluminum castings. Degassing operations remove the hydrogen gas from the molten aluminum. Gaseous emissions from HCE-based aluminum degassing have demonstrated high yields of complex organochlorine compounds, including HCB and OCS (Westberg et al., 1997).

G.2 CURRENT TOXICS RELEASE INVENTORY (TRI) STATUS

OCS is not currently reportable to TRI.

G.3 ESTIMATED NUMBER OF ADDITIONAL REPORTS TO TRI

This section estimates the number of TRI reports that may be submitted for OCS at various lower reporting thresholds. The reporting thresholds analyzed are 1 pound; 10 pounds; 100 pounds; and 1,000 pounds. The following estimates assume that the *de minimis* exemption would be eliminated; thus, TRI reporting is expected from facilities manufacturing, processing or otherwise using OCS above the reporting thresholds, regardless of the concentration.

G.3.1 ANALYTICAL METHODS

This subsection explains the methods used to estimate the number of additional facilities that may submit TRI reports for OCS at various lower reporting thresholds.

Although potential industrial sources of OCS have been identified, information is limited regarding the amount of OCS manufactured as a byproduct. For the industrial sectors without OCS data, hexachlorobenzene (HCB) was chosen as a surrogate to estimate the amount

of OCS manufactured as well as the number of potential TRI reports. HCB and OCS are structurally similar chemicals; both are a benzene ring surrounded by chlorine atoms. The difference between the two molecules is the substitution of a styrene molecule (carbon and hydrogen) for a chlorine atom at one of the benzene ring carbons. Based on the available information and the structural similarity of OCS and HCB, these chemicals appear to be manufactured as byproducts in many of the same processes. It is unknown whether OCS is also present as an impurity in products containing HCB as an impurity (e.g. chlorinated solvents). For this analysis, it is assumed that OCS does not remain with the manufactured product, but is removed with the process wastes.

Chemicals and Allied Products (SIC Code 28)

To estimate the number of facilities which may report OCS to TRI for various 4-digit SIC codes in the Chemicals and Allied Products Category, information on the amount of HCB and OCS produced in comparison to product yield for the manufacture of CTC and PCE by the Stauffer or Scientific Design processes (Markovee and Magee, 1984) was used. The ratio of OCS to HCB byproduct manufactured in SIC Code 2869 was then applied to the minimum quantities of HCB inferred from the TRI information (EPA, 1995b) to estimate the amount of OCS produced per facility in other 4-digit SIC codes.

The manufacture of CTC and PCE by the Stauffer or Scientific Design processes involves the chlorination of propylene, followed by distillation to separate and recover CTC and PCE. Under optimum conditions, 96 percent of the propylene is converted to CTC and PCE. The remaining 4 percent of propylene is converted to a byproduct residue termed “hex-waste”, of which HCB is a major component (assumed to be 75%). The other byproducts compose the remaining 25% of hex-waste, 22% of which is OCS (Markovee and Magee, 1984). Using the stoichiometric relationship between CTC and PCE manufacture from propylene and the waste generation and composition from the literature, approximately 0.0048 pounds of OCS byproduct is manufactured per pound of PCE manufactured. The calculated OCS:HCB production ratio is 0.073 lbs OCS/lb HCB from the CTC and PCE manufacturing process. The estimated concentration of OCS in the total amount of hex waste generated from the process is 5.5 percent.

From this information, the estimated amount of OCS from each facility in SIC code 2869 can be determined. Three facilities in SIC Code 2869 supplied enough PCE to meet a demand for 290 million pounds in 1997 (Chemical Marketing Report, 1997). Each facility therefore produces approximately 464,000 lb OCS as a byproduct per year, as shown below.

(290 million lb PCE/yr) x (0.0048 lb OCS / lb PCE) / (3 facilities) = 464,000 lb OCS/facility/yr

To determine which additional 4-digit SIC Codes in the Chemical and Allied Products category may manufacture OCS as a byproduct, and to estimate the amount per facility, the 1995 TRI reports for HCB were analyzed. According to the 1995 data, facilities in SIC codes 2812, 2865, and 2879 submitted TRI reports for the manufacture of HCB (EPA, 1995b). Using the TRI data, HCB production was estimated to be 25,000 lb per facility reporting in 1995 or the combined releases and off-site transfers of HCB, whichever amount was greater. Table G-1 presents a summary of estimated amount of HCB manufactured and the calculated OCS production amounts based on the CTC and PCE data for the three SIC codes. The estimated

amount of OCS manufactured on a per facility basis was estimated by dividing the total amount manufactured by the number of facilities in the SIC code. The amount of OCS per facility is provided in Table G-5 at the end of this section and was used to estimate the number of reports at the various thresholds.

TABLE G-1
ESTIMATED OCS MANUFACTURE
BASED ON HEXACHLOROBENZENE MANUFACTURE/RELEASES

SIC Code	Number of Reports	Estimated Amount of HCB Manufactured (lb/year) (EPA, 1995b)	OCS:HCB ratio	Estimated Amount of OCS Manufactured (lb/year)
2812	4	100,000	0.073	7,300
2865	1	25,000	0.073	1,800
2879	3	470,468[a]	0.073	34,300

[a]One facility reported 420,468 lb of HCB releases and off-site transfers for 1995 (EPA, 1995b). This facility is estimated to manufacture approximately 30,694 lb OCS as a byproduct.

The number of facilities that may submit TRI reports for OCS at various thresholds for SIC Code 2812 (alkalis and chlorine) were estimated from the Final Draft Report - Exposure Assessment for HCB (EPA, 1986). According to the report, only five chlorine manufacturing facilities in the United States had not converted from graphite (carbon) electrodes to metal electrodes by 1984. The 1995 TRI information shows that 4 chlorine manufacturing facilities had reported HCB manufacturing. This data indicates that at least 4, and possibly 5 chlorine manufacturing facilities are still using carbon electrodes and may submit TRI reports for OCS.

The number of facilities that may submit TRI reports for OCS at various thresholds for SIC codes 2865 and 2879 was estimated using the following method:

- Using the *Standard Industrial Classification Manual* (Executive Office of the President, 1987), those 5-digit SIC codes most likely to manufacture OCS as a byproduct were identified. Those SIC codes were 28651, 28652, 28653, 28655, 28656, 28795, 28796, 28797, 28798, and 28799.
- At the 4-digit SIC code level, the percentage of facilities in each identified SIC code having 10 or more full-time employees was obtained from the *1995 County Business Patterns* (Department of Commerce, 1995); and
- The number of facilities from the *1992 Census of Manufactures, Industry Series* (Department of Commerce, 1992) in each of the identified 5-digit SIC codes was multiplied by the calculated percentage of facilities in the corresponding 4-digit SIC code having 10 or more full-time employees.

The data for the steps outlined above are presented in Table G-2. By dividing the number of facilities shown in Table G-2 into the amount of OCS manufactured per year (Table G-1), the amount of OCS manufactured per year, and therefore the TRI reporting threshold can be determined. Because it is assumed that every facility in the 5-digit SIC code with 10 or more employees is manufacturing OCS as a byproduct, this estimation method results in a high-end estimate of the number of reports at various thresholds.

TABLE G-2
ESTIMATED NUMBER OF FACILITIES POTENTIALLY PRODUCING OCS FROM SELECTED MANUFACTURING SECTORS

Industry Description	SIC Code[a]	Total Facilities in 5-Digit Code[b]	Total Facilities in 4-Digit Code[c]	Facilities with ≥10 Employees in 4-Digit Code[c]	% of Total Facilities with ≥10 Employees in 4-Digit Code	Estimated Facilities with ≥10 Employees in 5-Digit Code
Cyclic Organic Crudes and Intermediates, and Organic Dyes and Pigments	2865	149	209	165	79	118
Pesticides and Agricultural Chemicals	2879	127	242	144	60	76

n.e.c. - not elsewhere classified
NA - Information was not available
Sources:
[a] Executive Office of the President, 1987
[b] Department of Commerce, 1992.
[c] Department of Commerce, 1995.

Magnesium Production (SIC Code 3339)

OCS has been identified as a potential byproduct of metallic magnesium production from magnesium chloride using carbon electrodes. According to the literature, annual OCS byproduct manufacture was estimated between 130 and 180 pounds from one facility located in Norway (Knutzen and Oehme, 1989). The actual concentration of OCS in the process wastes is unknown. Assuming that the magnesium plant in Norway was similar in size to the two US metallic magnesium producers, then between 260 and 360 pounds per year of OCS byproduct is expected from this process. Therefore, the two US metallic magnesium producers may report to TRI at thresholds of 1 pound, 10 pounds, and 100 pounds.

Aluminum Production (SIC Codes 3341 and 3365)

OCS is manufactured as a byproduct in the aluminum production industry when HCE is used to remove hydrogen gas from molten aluminum (Westberg et al., 1997). Quantitative information on the amount of OCS produced in comparison to the amount of HCE used was available from the literature (Westberg et al., 1997). This information was used to estimate the amount of OCS generated by the degassing process. According to The Aluminum Association (1998), five secondary aluminum smelting operations in the U.S. use HCE for degassing; this information was used to estimate the number of primary aluminum foundries that may use HCE for degassing.

According to the literature, a remelt furnace was charged with 70 kg of an aluminum alloy and degassed using two 50 g tablets containing 85% HCE (Westberg et al., 1997). This results in a ratio of 0.00121 lb HCE/lb aluminum alloy, as shown below.

$$(2 \times 50 \text{ g HCE} \times 85\%) / 70{,}000 \text{ g alloy} = 0.00121 \text{ g HCE / g alloy} = 0.00121 \text{ lb HCE / lb alloy}$$

Analysis of the emissions from the process detected 0.78 mg OCS per gram of HCE (Westberg et al., 1997). Using this information, an OCS:aluminum alloy ratio of 9.44×10^{-7} was calculated and is shown below.

$$(7.8 \times 10^{-4} \text{ g OCS / g HCE}) \times (0.00121 \text{ g HCE / g alloy}) = 9.44 \times 10^{-7} \text{ lbs OCS/lb aluminum alloy}$$

To estimate the number of aluminum foundries using HCE in degassing, the percentage of secondary smelting plants using HCE in degassing was applied to the number of aluminum foundries. These data are presented in Table G-3.

TABLE G-3
ESTIMATED NUMBER OF ALUMINUM FOUNDRIES
USING HCE DEGASSING OPERATIONS

SIC Code	Total Foundries[a]	Total Secondary Smelting Facilities[a]	Secondary Smelting Facilities Using HCE[b]	% of Total Secondary Smelting Facilities Using HCE	Estimated Foundries Using HCE
3365	591	72	5	7	41

Sources:
[a]Department of Commerce, 1992
[b]EPA, 1993

The amount of aluminum produced by secondary smelting facilities using HCE was available from The Aluminum Association (1998); however, only the total primary aluminum production was available from the listed references. Assuming that the foundries produce approximately equal amounts of aluminum each year, a scaling factor of 7% (calculated above) was applied to estimate the amount of primary aluminum production using HCE degassing operations. Table G-4 presents the estimated amount of OCS manufactured by the primary and secondary aluminum industry.

TABLE G-4
ESTIMATED ALUMINUM INDUSTRY OCS MANUFACTURE

SIC Code	Estimated Amount of Aluminum Manufactured (million lb/year)	OCS:Aluminum ratio	Total Estimated Amount of OCS Manufactured (lb/year)
3341	108[a]	9.44×10^{-7}	102
3365	556[b]	9.44×10^{-7}	525

Sources:
[a]Aluminum Association, 1998 (converted from 53,922 tons)
[b]3,600,000 metric tons aluminum (USGS, 1998) x (2,205 lb / metric ton) x 7% using HCE = 556,000,000 lb aluminum using HCE

Commercial Hazardous Waste Treatment (SIC Code 4953)

OCS may be generated at incineration facilities during the thermal decomposition of plastic wastes. As indicated in the economic analysis of EPA's recent TRI industry expansion (EPA, 1997) 53 hazardous waste incinerators are now subject to the TRI reporting requirements. All of these incinerators are assumed to generate OCS in quantities exceeding the four regulatory options, but below current reporting thresholds.

Other Industry Sectors

The dry etching of aluminum conductors with CTC or boron trichloride for microelectronic components (SIC code 367) has been demonstrated to produce OCS byproduct (Raabe et al., 1993). Samples collected from a reactor contaminated with waste products from etching operations were composed of 0.6% OCS (Raabe et al., 1993). Quantitative information

is not currently available to estimate the total amount of OCS produced by aluminum etching or the number of facilities producing OCS by this process.

There may be a potential for incidental manufacturing of OCS at pulp mills (EPA, 1998); however, the pulp and paper industry has been drastically reducing its use of chlorine bleaches. Therefore, no pulp mills (SIC code 2611) were included in estimates of OCS reports to TRI.

Medical waste incinerators are not currently required to submit reports to TRI; however, they are considered to be potential producers of OCS through incineration of polyvinyl chloride (PVC) plastics.

There is a potential for OCS formation at cement kilns incinerating hazardous wastes. Based on professional knowledge of the industry, however, cement kilns are not expected to submit reports to TRI for OCS.

Summary

Industries manufacturing OCS that may submit TRI reports at the lowered thresholds are presented in Table G-5, along with the results of the analysis. Note that the table is presented in two parts since it is oversized. The first six columns are presented for all SIC codes followed by the last seven columns for all SIC codes. The last four columns provide the number of facilities expected to report to TRI at the various thresholds. The number of facilities expected to report at the various thresholds in the last four columns was determined from the amount of OCS manufactured per facility.

TABLE G-5
ESTIMATES OF ADDITIONAL TRI REPORTING FOR OCTACHLOROSTYRENE (OCS)

Industries	OCS Purpose/Use	TRI Activity Category	Total Amount of OCS (lb/yr)	No. of Facilities with >10 FTEs Potentially Subject to TRI Reporting Requirements	Amount per Facility (lb/yr)
Alkalies and Chlorine (SIC Code 2812)	Formed as a byproduct/impurity during electrolysis of chloride salts such as sodium chloride and magnesium chloride using carbon anodes (16)	Manufacture	7,300 (8, 17)	5 (20)	1,460
Cyclic Organic Crudes and Intermediates, and Organic Dyes and Pigments (SIC Code 2865)	Formed as a byproduct/impurity during chlorination of various organic compounds (16)	Manufacture	1,800 (8, 17)	1[a] (17) - 118 (11, 12)	15 - 1,800
Industrial Organic Chemicals, n.e.c. (SIC Code 2869)	Formed as a byproduct/impurity during chlorination of various organic compounds (including propylene in the production of carbon tetrachloride and tetrachloroethylene by the Stauffer or Scientific Design processes) (8, 16, 17)	Manufacture	1,392,000 (8, 22)	3 (2)	464,000
Pesticides and Agricultural Chemicals, n.e.c. (SIC Code 2879)	Formed as a byproduct/impurity during pesticide manufacturing (16)	Manufacture	34,300 (8, 17)	3[a] (17) - 76 (11, 12)	> 30,000 (1 facility) < 1,000 (75 facilities) (17)
Chemicals and Allied Products TOTAL (SIC Code 28)			**1,435,000**	**12 - 202**	

TABLE G-5 (Continued)
ESTIMATES OF ADDITIONAL TRI REPORTING FOR OCTACHLOROSTYRENE (OCS)

Industries	OCS Purpose/Use	TRI Activity Category	Total Amount of OCS (lb/yr)	No. of Facilities with >10 FTEs Potentially Subject to TRI Reporting Requirements	Amount per Facility (lb/yr)
Primary Smelting and Refining of Nonferrous Metals, Except Copper and Aluminum (SIC Code 3339)	Formed as a byproduct during the electrolytic production of metallic magnesium using carbon electrodes.	Manufacture	260-360 (6)	2 (25)	130-180
Secondary Smelting and Refining of Nonferrous Metals (SIC Code 3341)	Formed as a byproduct/impurity during degassing of molten aluminum with hexachloroethane (23)	Manufacture	100 (23, 24)	5 (24)	20
Aluminum Foundries (SIC Code 3365)	Formed as a byproduct/impurity during degassing of molten aluminum with hexachloroethane (23)	Manufacture	530 (21, 23)	41 (12, 23)	13
Primary Metal Industries TOTAL (SIC Code 33)			**890-990**	**48**	
Electroplating, Plating, Polishing, Anodizing, and Coloring (SIC Code 3471)	Formed as a byproduct/impurity during dry etching of aluminum with carbon tetrachloride or boron trichloride (10)	Manufacture	unknown[b]	unknown	unknown[b]
Refuse Systems (SIC Code 4953)	Received in waste streams	Otherwise Used	1,341,000	162 (14)	>1,000
TOTAL			**1,436,000**[c]	**222 - 412**	

TABLE G-5 (Continued)
ESTIMATES OF ADDITIONAL TRI REPORTING FOR OCTACHLOROSTYRENE (OCS)

Industries	OCS Concentrations in Waste	Number of Facilities Reporting to TRI at Current Threshold	Number of Additional Reports Expected at Various Thresholds			
			>1 lb/yr	>10 lb/yr	>100 lb/yr	>1,000 lb/yr
Alkalies and Chlorine (SIC Code 2812)	5.5% (8)	NA	5	5	5	5
Cyclic Organic Crudes and Intermediates, and Organic Dyes and Pigments (SIC Code 2865)	5.5% (8)	NA	118	118	1 - 118	1
Industrial Organic Chemicals, n.e.c. (SIC Code 2869)	5.5% (8)	NA	3	3	3	3
Pesticides and Agricultural Chemicals, n.e.c. (SIC Code 2879)	5.5% (8)	NA	76	3 - 76	3	3
Chemicals and Allied Products TOTAL (SIC Code 28)		**NA**	**202**	**129 - 202**	**12 - 129**	**12**
Primary Smelting and Refining of Nonferrous Metals, Except Copper and Aluminum (SIC Code 3339)	Unknown	NA	2	2	2	0
Secondary Smelting and Refining of Nonferrous Metals (SIC Code 3341)	0.078%[e] (23)	NA	5	5	0	0

TABLE G-5 (Continued)
ESTIMATES OF ADDITIONAL TRI REPORTING FOR OCTACHLOROSTYRENE (OCS)

Industries	OCS Concentrations in Waste	Number of Facilities Reporting to TRI at Current Threshold	Number of Additional Reports Expected at Various Thresholds			
			>1 lb/yr	>10 lb/yr	>100 lb/yr	>1,000 lb/yr
Aluminum Foundries (SIC Code 3365)	0.078%[e] (23)	NA	41	41	0	0
Primary Metal Industries TOTAL (SIC Code 33)		**NA**	**48**	**48**	**2**	**0**
Electroplating, Plating, Polishing, Anodizing, and Coloring (SIC Code 3471)	0.6% (10)	NA	0	0	0	0
Refuse Systems (SIC Code 4953)	unknown[d]	NA	53	53	53	53
TOTAL		**NA**	**303**	**230-303**	**67-184**	**65**

TABLE G-5
ESTIMATES OF ADDITIONAL TRI REPORTING
FOR OCTACHLOROSTYRENE (OCS)

Footnotes

NA - not applicable
n.e.c. - not elsewhere classified

a - The low end of the range is the number of facilities in the 1995 TRI database (EPA, 1995b) that claim the 4-digit SIC code as their primary manufacturing description and that manufacture hexachlorobenzene as a byproduct or impurity.

b - OCS may be generated in these industries; however, the literature search did not show any information regarding the quantity generated. Additionally, no facilities in this SIC code filed TRI reports for HCB. Further research is required to estimate this quantity.

c - The total amount of OCS does not include the amount of OCS received by treatment, storage, and disposal facilities (TSDFs) to avoid double counting.

d - There are no available data on typical concentrations expected for OCS.

e - The OCS concentration is based on the amount of hexachloroethane used for degassing.

G.4 CONCLUSIONS

As a result of lowering the TRI reporting thresholds and adding OCS to the TRI, the estimated total number of reports for OCS at the various lower thresholds are summarized below. It should be noted that there is considerable uncertainty regarding potential sources and amounts of OCS.

- 1 lb/yr - 303;
- 10 lb/yr - 230 to 303;
- 100 lb/yr - 67 to 184; and
- 1,000 lb/yr - 65.

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HALOGENATED SOLVENTS INDUSTRY ALLIANCE, INC.
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August 4, 1998

Mr. Eric Ginsburg
Office of Air Quality Planning and Standards (MD-15)
Air Quality Strategies and Standards Division
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Re: Source Category Listing for Section 112(d)(2) Rulemaking Pursuant to Section 112(c)(6) Requirements (63 *Federal Register* 17838, April 10, 1998)

Dear Mr. Ginsburg:

The Halogenated Solvents Industry Alliance, Inc. (HSIA) remains very concerned about the Agency's mischaracterization of the contribution to hexachlorobenzene (HCB) emissions of the production of trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, carbon tetrachloride and ethylene dichloride in its inventory of Section 112(c)(6) pollutants. Although we appreciate that EPA is not proposing to take further action to control chlorinated solvents production, we believe that it is important that the inventory accurately reflect the available emissions information for these sources. HSIA is a trade association representing the manufacturers and many users of several chlorinated solvents. These comments supplement those we made in response to the Agency's draft inventory published on June 20, 1997.

HSIA's concerns about the characterization of the contribution of chlorinated solvent production to the HCB emission inventory are two-fold. First, the Agency has decided to exclude the two largest sources of HCB emissions -- pesticide application and utility coal combustion -- from the 112(d)(2) inventory. Second, the Agency's estimates for chlorinated solvents production are based on a flawed extrapolation from a small number of facilities.

Exclusion of Pesticide Application and Utility Coal Combustion

The result of excluding the two largest sources is the suggestion that the remaining sources, including chlorinated solvents production, contribute significantly to HCB emissions when they are actually quite small in comparison. In fact, according to the 1993 report by TRC Environmental that is the basis for EPA's estimate of emissions from solvent production, emissions from the application of certain pesticides dwarfs all other sources.

EPA has explained its rationale for excluding pesticide application from the inventory, but has not explaincd the significant difference between the estimate of 404,197 pounds from the TRC report and that of 292 pounds in the April 1998 inventory. Moreover, EPA's April 1998 final report notes that more recent data suggest that pesticide application emissions are actually lower than the estimate used. Similar data have been provided for chlorinated solvent production by HSIA in response to the June 20, 1997 *Federal Register* notice, but are not referenced in the April 1998 report.

HSIA disagrees, moreover, with the Agency's decision not to credit possible reductions in emissions from utilities achieved as a result of implementation of Section 112(n)(1)(A) in the 112(c)(6) process. While the statutory language does not require EPA to control emissions of utilities to address the 112(c)(6) pollutants, it clearly does not preclude EPA from doing so nor from taking credit for reductions achieved under other requirements of Section 112. Although 112(n)(l)(A) may be the appropriate authority for evaluating utility emissions, any reductions achieved under that authority should be taken into account in the inventory of source categories for 112(c)(6) pollutants. This is particularly true since any controls on utilities likely will be implemented through 112(d).

Overestimate of Emissions from Chlorinated Solvents Production

In its July 21, 1997 comments, HSIA provided data concerning actual measurements of HCB emissions from chlorinated solvents production. In response to these comments, the Agency argued that its estimates are preferable because they are based on industry-reported emissions from the 1990 Toxic Release Inventory (TRI) database. In fact, however, only six of the 21 solvents production facilities identified by EPA reported HCB emissions in their 1990 TRI reports. Emissions for the remaining 15 facilities, accounting for 55 percent of the total estimate for the category, were based on extrapolations from the six facilities

and the production capacity. The information submitted by HSIA, moreover, suggests that the TRI data for the six facilities may have significantly overestimated actual HCB emissions.

All of the 15 facilities for which emissions were estimated submitted TRI reports for 1990, but did not report emissions of HCB. Neither the contractor nor EPA has provided the rationale for concluding that these companies were in error by not reporting HCB emissions. HSIA, on the other hand, has provided a rationale for concluding that HCB emissions from these facilities may actually be zero. The contractor and EPA also fail to provide any basis for assuming that emissions from these 15 facilities would be similar to the other six, or why production capacity, rather than actual 1990 production, was used. Production numbers for the solvents of interest for 1990 are readily available and could be easily apportioned among the manufacturing facilities, if necessary.

HSIA has reviewed the TRI reporting for several of the 15 facilities whose emissions were estimated. The largest contributor -- AKZO in Alabama (an estimated 222 pounds) -- has not reported HCB emissions in any of its TRI reports since 1990. The next largest contributor -- Occidental Chemical in Texas (an estimated 123 pounds) reported 25 pounds of HCB emissions in 1991, but not in any subsequent year. Two other facilities that HSIA investigated -- Westlake Monomers in Kentucky (an estimated 20 pounds) and Formosa Plastics in Louisiana (an estimated 10 pounds) -- also have not reported HCB emissions in their TRI reports in any year since 1990. One of these companies -- Westlake Monomers -- reported releases of HCB in 1991 through 1995, but none were to the air.

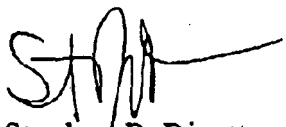
While defending the use of extrapolations for chlorinated solvent production, the Agency acknowledges that it based emissions for another identified source category, pesticide manufacture, solely on the emissions reported under the TRI requirement. In the April 1988 final inventory report, EPA makes no attempt to extrapolate to other manufacturing facilities, as it did for chlorinated solvent production, despite acknowledging that it is “probable” that emissions from pesticide manufacture are underestimated. This acknowledgment, moreover, is not discussed in the April 10, 1998 notice.

Summary

In summary, HSIA believes that the final HCB inventory incorrectly overemphasizes emissions from chlorinated solvents production by (1) eliminating the two largest sources of HCB emissions from the inventory and (2) inappropriately estimating emissions from 15 of the 21 manufacturing facilities. We believe that the Agency must correct these problems to more accurately reflect the inventory of HCB emissions. Without such corrections, an uninformed reader would incorrectly conclude that chlorinated solvent production is a significant source of HCB.

We would like to discuss this matter further with you and your staff. Perhaps the next step would be a meeting of EPA and HSIA representatives who have the relevant technical expertise. I will plan to call you in the next couple of weeks to discuss such a meeting. Please feel free to call me in the meantime.

Sincerely,



Stephen P. Risotto
Executive Director

cc: Patrick Chang, EPA/OGC

Comments Received from PTF

February 26, 1999

Via Facsimile & E-mail

Mr. Frank Anscombe
U.S. Environmental Protection Agency
77 W. Jackson Boulevard
Chicago, IL 60604

RE: Octachlorostyrene Sources

Dear Mr. Anscombe:

I am writing on behalf of the Pentachlorophenol Task Force ("PTF") to comment on the draft report entitled "Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources" (hereinafter "OCS Report") (dated December 22, 1998). The PTF has been organized to support the continued registration of pentachlorophenol ("penta") in the U.S., Canada and elsewhere. It is comprised of the two U.S. registrants of penta – Vulcan Chemicals, a business unit of Vulcan Materials Company, and KMG-Bernuth Inc. ("KMG"). As part of its charter, the PTF is committed to ensuring that regulatory decision implicating penta are based on sound science and reflect current, up-to-date data.

1 Page 50 of the draft OCS Report states that the production of penta is suspected of forming octachlorostyrene ("OCS") as a byproduct in trace amounts. A citation to Kirk-Othmer 1996 is given in support of that statement. The authors of the OCS Report attempt to draw a parallel between PCDD/PCDF formation during penta manufacture and OCS formation. Indeed, Table 4 of the draft report goes so far as to suggest that the amount of penta used annually to treat utility poles may contain up to 16,325,000 grams of OCS. Based on roughly the 17 million pounds of penta being produced annually by PTF member companies, the figure in the Table would translate to an OCS content in penta of approximately 0.4 percent.

2 The PTF members have no information confirming the presence of OCS in penta, as is suggested in the OCS Report. Nonetheless, we fail to see the scientific rationale for drawing a connection between the formation of trace quantities of certain higher chlorinated PCDDs/PCDFs during penta manufacture with any possible OCS formation. We have examined the Kirk-Othmer

reference and fail to see how that supports the contentions in the OCS Report.

Moreover, the suggestion that penta contains up to 0.4 percent OCS is plainly wrong. PTF member Vulcan has analyzed its penta for the presence of any contaminants at levels above 0.1 percent and in those analyses OCS has not been identified.

If you have any questions, do not hesitate to call me.

Sincerely,

John Wilkinson

RUBBER manufacturers association

1400 K Street, NW • Washington, DC 20005 • tel (202) 682-4800 • fax (202) 682-4809 •

March 11, 1999

Mr. Frank Anscombe
U.S. Environmental Protection Agency
Region 5 (G-17J)
77 West Jackson Boulevard
Chicago, IL 60604

Mr. Darryl Hogg
Canada Ontario Agreement Coordination
Ministry of Environment
40 St. Clair Avenue West, 12th Floor
Toronto, Ontario M4V 1M2

Dear Mr. Anscombe and Mr. Hogg:

On behalf of the members of the Rubber Manufacturers Association (RMA), I am pleased to provide the Great Lakes Binational Toxics Strategy (BNTS) OCS Workgroup with RMA's comments on the Battelle Memorial Institute draft report entitled *Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources* (hereinafter referred to as the "draft report"), dated December 22, 1998.

The Rubber Manufacturers Association is the national trade association for the rubber products industry, and represents a $50 billion domestic manufacturing sector. RMA represents more than 120 companies that manufacture various rubber products, including tires, hoses, belts, seals, molded goods, and other finished rubber products.

A*s mentioned in the comments filed by the Council of the Great Lakes Industries on the draft report, RMA has serious concerns about the analysis and characterization of the tire industry as a potential source of OCS. In particular, RMA does not believe that tire manufacturing operations are a source of either hexachlorobenzene (HCB) or OCS emissions, based on the raw materials and physical and reaction chemistry present in tire manufacturing. RMA is planning to conduct emissions testing to show that HCB is not emitted during the tire

manufacturing process, and will present the results to RMA upon the completion of the emission testing.

The tire industry is willing to work with you to provide accurate information regarding the tire manufacturing process. Please feel free to contact me with any questions regarding these comments. I may be reached at 202-682-4839 or via e-mail at tracey@rma.org.

Sincerely,

Tracey J. Norberg
Director, Environmental Affairs

Cc: George Kuper, CGLI
Dale Phenicie, CGLI
Tony Wayne, EPA OAQPS
Dale Evarts, EPA OAQPS
Laurel Driver, EPA OAQPS

Rubber Manufacturers AssociationComments on the
Draft Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report

Introduction

The Battelle Memorial Institute issued a draft report on December 22, 1998 entitled *Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources* (hereinafter referred to as the "draft report") to US EPA's Great Lakes National Program Office. The Rubber Manufacturers Association (RMA) is pleased to submit comments on the draft report.

The Rubber Manufacturers Association is the national trade association for the rubber products industry, and represents a $50 billion domestic manufacturing sector. RMA represents more than 120 companies that manufacture various rubber products, including tires, hoses, belts, seals, molded goods, and other finished rubber products.

RMA is concerned with the characterization of the tire industry in the draft report and disagrees with the analysis of the tire industry. In particular, RMA believes that it is extremely unlikely or impossible for tire manufacturing to emit OCS. RMA bases this belief on the industry's knowledge of its manufacturing processes – specifically that tire manufacturing does not have sufficient radical chlorine or elevated temperatures to form OCS. In addition, RMA does not believe that tire manufacturing is a source of hexachlorobenzene (HCB) emissions, and plans to conduct testing to support this belief.

Basis for EPA Contractor's Position

In the draft report, rubber tire manufacturing operations have been identified as a potential source of OCS. As is explained below, the Rubber Manufacturers Association (RMA) disagrees with the draft report's analysis of the tire manufacturing industry and believes it is extremely unlikely or even impossible that OCS is emitted from tire manufacturing operations. We base our belief on several facts and our knowledge of the rubber tire manufacturing process.

RMA recognizes that the draft report does not purport to definitively identify sources of OCS. In fact, the draft report notes "the *scarcity of data* characterizing OCS emissions," and also points out that the Battelle study "was conducted as a *tentative gauge* of OCS emissions for selected potential sources and is *presented for discussion purposes only*." Draft report at page v (emphasis added). Yet the draft report recites several erroneous points, and therefore draws the incorrect tentative conclusion that OCS may be formed during the tire manufacturing process.

This inappropriate tentative conclusion is based on the following (sometimes inaccurate) assumptions outlined by Battelle in the draft report (Reference section 4.21 on page 51):

1. EPA recently – and in our view, incorrectly – identified rubber tire manufacturing as a source of hexachlorobenzene (HCB) emissions; and

2. The draft report makes what we believe to be several incorrect statements in the passage quoted below:

> Several steps in the tire manufacturing process show potential for generating OCS (including the mixing, milling, extruding, calendering, curing, and cementing operations). Carbon black is one of the ingredients in the rubber compound used to manufacture various components required in the production of rubber tires. Natural rubber contains chlorine. The mixing step combines raw materials, including carbon black in a mixer with the use of vulcanizing agents, plasticizers, and initiators. During milling, the rubber compound is heated to a fluid in preparation for extruding. Extruding shapes the rubber into profiles by forcing the hot fluid through dies. The calendering process uses hot rubber from the mills and forms it into fibers or thin sheets of rubber and rubber-coated materials. Curing presses and molds the various components of a tire together under high temperature and pressure. Prior to curing, an uncured tire is sprayed with a lubricant so that the tire does not adhere to the mold during curing. Cementing is the use of adhesives or solvents at various stages of tire building to improve adhesion of rubber components and prevent separation prior to curing. Due to the high temperature and presence of organic materials, OCS may be formed. *Draft Report at 51.*

RMA disagrees with the Battelle/EPA contention that rubber tire manufacturing is a source of OCS. The logic behind RMA's reasoning is described below.

1 Rubber Tire Manufacturing is not a Source of HCB Emissions

RMA is confident that HCB is not emitted during any tire manufacturing processes and is planning to conduct emissions testing soon to demonstrate this point. While EPA's current emissions inventories for the Clean Air Act section 112(c)(6) pollutants identify tire manufacturing as a source of HCB, these inventories are based solely on a single data point that RMA believes to be erroneous.

In 1994 and 1995, the rubber manufacturing industry completed a detailed study of emissions from its various process (mixing, milling, extruding, calendering, and curing) to help develop AP-42 factors for the industry. This study involved testing 23 generic rubber compounds representing a range of materials processed in the entire rubber industry. During the rubber-mixing portion of this study, HCB was detected during a single test of the emissions from one compound, Compound #3. RMA believes that this data point is not valid and that the HCB detection was caused by contamination of the emission sample. This belief is based on the fact that HCB is a common contaminant introduced by the thermal degradation of the adsorbent resin (XAD II) used for sampling. In addition, HCB was not detected in the emissions from any of the other 22 compounds tested in mixing and in none of the compounds tested in the other tire manufacturing processes (milling, extruding, calendering, and curing). Compound #3 was tested in the milling process, and HCB was not detected.

As will be discussed below, no physical or chemical mechanism for HCB formation exists within rubber tire manufacturing. RMA therefore is preparing to conduct additional tests this spring to demonstrate that this data point is not valid, and that HCB is not emitted during tire manufacturing. The results of these tests will be shared with EPA when they become available in the summer of 1999. Because the draft report's speculation about the presence of OCS in tire manufacturing processes is premised in large part on the presence of HCB, we believe that test results demonstrating the absence of HCB should lead EPA to conclude that OCS also is not emitted during tire manufacturing.

EPA HCB Emissions Inventory for Rubber Tire Manufacturing

Even if the single HCB data point was not due to testing contamination, the erroneous HCB emissions inventory calculation performed by US EPA in its *1990 Emissions Inventory Of Section 112(c)(6) Pollutants: POM, TCDD, TCDF, PCBs, HCB, Hg and Alkylated Pb, Final Report* issued April 1998, greatly inflated the estimate of HCB emissions from the industry. In that report EPA indicates that total national HCB emissions for the Tire Manufacturing industry are 869 pounds (reference Table 7-3). EPA based this calculation on information found in Table 7-1 of the report. Table 7-1 contains information that was purportedly obtained from the MACT standards program. A review of this information reveals that, even if one believed the single HCB data point to be valid, EPA has significantly overestimated HCB emissions for the industry. EPA has apparently attempted to perform an HCB emissions calculation estimate for the industry using obsolete data and incorrect calculating methodologies.

Emissions factors for the tire industry reside on EPA's AP-42 web site found at www.epa.gov/ttn/chief/ap-42dsur.html. At this location current HCB emissions factors are noted as follows:

Mixing Compound #3 = 9.29E-09 lb/lb rubber;
Milling Compound #3 = non-detect;
Extruder Compound #3 = 4.98E-09 lb/lb rubber (*interpolated from single mixing data point*);
Calendering Compound #3 = 6.74E-09 lb/lb rubber (*interpolated from single mixing data point*); and
Tire Curing = non-detect for all tires tested

As noted above, HCB was not detected in any other compound tested. It needs to be reiterated at this point that the above values are based on what the industry believes to be an invalid data point, which will be reevaluated shortly through additional emission testing.

Regardless of concerns about the accuracy of these emission factors, when estimating HCB emissions using the above emissions factors EPA must also consider that Compound #3 represents a single tire compound representing about 15% of the rubber actually used in tire manufacturing. It is also important to note that compound #3 is processed through mixing, calendering and/or extruding or milling depending on the equipment configuration used to feed

rubber to the calender. In addition, Compound #3 is cured as part of the tire curing process, but HCB was not detected during any tire curing emission tests.

Using the annual U.S. tire production number found in Table 7-1 of EPA's report (264,262,000 tires produced), and assuming (a) an average tire weight = 25 pounds; (b) rubber content per tire = 85%; (c) amount of Compound #3 per tire = 15%; and (d) the validity of the single data point showing the presence of HCB is valid; one can estimate HCB emissions as follows:

Amount of Compound #3 needed for production:

(264,262,000 tires)x(25 lb/tire)x(90%)x(15%) = 891,884,250 lbs of Compound #3 needed annually

HCB Emissions Estimate for Rubber Mixing Calculation:

(891,884,250 lb rubber)x(9.29E-09 lb HCB/lb Rubber) = 8.3 pounds HCB from Mixing

Estimated HCB Emissions from Rubber Calendering (assuming an extruder pass is used to feed the rubber to the calender – worst case):

(891,884,250 lb rubber)x(4.98E-09 + 6.74E-09 lb HCB/lb rubber) = 10.5 pounds HCB from Calendering operation

Since there are no emission factors for milling or curing, the total HCB emissions would be estimated as follows:

8.3 pounds from mixing + 10.5 pounds from calendering operations = 18.8 pounds HCB (total estimated annual nationwide emissions)

This 18.8 pounds total figure is dramatically less than EPA's estimate of 869 pounds found in Table 7-3 of the 112(c)(6) inventory. The RMA would like to discuss the above HCB emission estimate calculation methodology with EPA. Moreover, as indicated above, the RMA believes that the basis for these calculations, the HCB mixing emission factor for Compound #3 is incorrect and the actual HCB emissions from tire manufacturing are zero. Additional testing will be conducted to confirm this belief.

2 HCB and OCS Cannot be Formed in Rubber Tire Manufacturing

The Battelle report theorizes that HCB and OCS are formed during rubber tire manufacturing. As noted above, the report states that natural rubber contains chlorine and that chlorine combines with carbon and other organic ingredients used in tire manufacturing to form HCB and OCS. However, it is apparent that Battelle has not recognized that two key aspects of the BCB/OCS formation mechanism are not present in tire manufacturing; i.e. the presence of *radical* chlorine and elevated temperatures.

Section 4.1 of the draft report attempts to identify mechanisms for formation of HCB and OCS. A discussion of a "de novo synthesis reaction" is outlined. This discussion of the reaction mechanism contends that elemental carbon and chlorine can combine at elevated temperatures (600-800ºC) and moderate pressure to produce the precursors of HCB and OCS. As the reaction mechanisms continue, smaller chlorinated organic molecules combine to form HCB and OCS. The draft report has linked this mechanism to industries or processes that operate at extremely high temperatures (incinerators, smelters, fuel combustion, etc.) and which commonly involve the presence of highly chlorinated materials. However, the draft report fails to recognize the nature of the processes and operating conditions found in the rubber tire manufacturing industry – and thus draws incorrect conclusions based upon these misunderstandings of the manufacturing process.

A review of the rubber tire manufacturing process reveals that the first of the required elements needed for the chlorination reactions to occur, namely, chlorine. The RMA does not believe that chlorine is present in significant concentrations in natural rubber. If natural rubber does contain chlorine it is likely to be present in extremely small trace amounts and in a form not readily available for the type of reaction chemistry needed to form HCB and OCS. The "de novo synthesis reaction" requires atomic chlorine radicals to be present to react with carbon and other organic molecules. This type of chlorine is not present in rubber tire manufacturing. In addition, tire manufacturing does not involve the type of conditions required to generate atomic chlorine radicals; i.e., extremely elevated temperatures.

Furthermore, the temperatures involved in tire manufacturing are too low for the "de novo synthesis reaction" to occur. Rubber mixing, milling, extruding, and calendering operations in tire manufacturing are typically conducted at temperatures less than 121 ºC. Tire curing operations are typically conducted at less than 175 ºC. These temperatures are significantly lower than the minimum temperature range required for the "de novo synthesis reaction" mechanism to occur, which is 600-800 ºC. Without such elevated temperatures, the reaction chemistry simply cannot occur. Since the temperatures involved in tire manufacturing are significantly less than 600 ºC, the "de novo synthesis reaction" cannot occur in tire manufacturing and HCB/OCS cannot be formed by this mechanism. The Battelle report does not offer another mechanism for HCB and OCS formation in tire manufacturing.

3 General Tire & Rubber Facility – Ashtabula, Ohio

Table 3 of the Battelle report lists Potential Industrial Sources of OCS in the Great Lakes Basin. The table includes a tire manufacturing facility, owned by General Tire & Rubber, located in Ashtabula, Ohio. The RMA is not familiar with such a facility and requests that EPA provide additional information into the location and type of operation conducted at this source so that a proper assessment of its true impact can be evaluated.

Summary

As indicated above, the RMA believes that rubber tire manufacturing is not a source of HCB emissions. Although HCB was detected in the mixing emissions from one rubber compound tested, the RMA believes that the detection was a result of laboratory contamination. Additional testing is being planned. Moreover, the chemistry and temperatures involved do not provide for the formation of HCB and OCS in tire manufacturing. Consequently, the RMA concludes that tire manufacturing is not a source of HCB or OCS impact on the Great Lakes. Therefore, RMA respectfully requests that EPA remove rubber tire manufacturing from its list of possible OCS sources. RMA and its members would be happy to discuss the matters raised in this paper so that EPA has a full understanding of the rubber tire manufacturing process and why it is highly improbable or impossible that HCB or OCS would be emitted from this process.

The Vinyl Institute

A Business Unit of The Society of the Plastics Industry, Inc.

March 1, 1999

Via **Facsimile**
Elizabeth Laplante
Frank R. Anscombe
Region 5, U.S. Environmental Protection Agency
Mail Code G-17J
77 West Jackson Boulevard
Chicago, IL 60604-3507

Re: SPI Vinyl Institute; Comments on Draft Great Lakes Binational Toxics Strategy Octachlorostyrene Report: A Review of Potential Sources

Dear Ms. Laplante and Mr. Anscombe:

Please find enclosed comments of the Vinyl Institute, a business unit of The Society of the Plastics Industry, Inc. (SPI), on the U.S. Environmental Protection Agency's (EPA) *Draft Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review ofPotential Sources.* 63 *Fed Reg.* 72,311 (1998).

Members of the VI are responsible for the majority of the domestic production volume of ethylene dichloride (EDC), vinyl chloride monomer (VCM) and polyvinyl chloride (PVC). Consequently, VI is responding to the suggestion that technologies employed by the vinyl industry or its products ultimately produce octachlorostyrene, an industrial byproduct that is viewed as a persistent bioaccumulative toxic (PBT) contaminant that poses a threat to the Great Lakes Basin environment. As discussed in the comments, for a number of reasons, the VI does not believe that the vinyl industry has any real impact on the Great Lakes Basin.

Again, the VI appreciates the opportunity to comment on the Draft OCS Report, and would be pleased to further discuss its analyses with you. Please do not hesitate to contact us if you have any questions.

Sincerely,

Frank E. Borrelli/PLD

Frank E. Borrelli
Technical Director

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Enclosure

cc: William F. Carroll, Jr., OxyChem
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COMMENTS OF THE SPI VINYL INSTITUTE

The Vinyl Institute (VI), a business unit of The Society of the Plastics Industry, Inc. (SPI), is pleased to provide comments on the December 22, *1998, Draft Great Lakes Binational Toxics Strategy Octachlorostyrene (OCS) Report: A Review of Potential Sources.* Specifically, the VI is responding to the suggestion that technologies employed by the vinyl industry or its products ultimately produce octachlorostyrene (OCS), an industrial byproduct that is viewed as a persistent bioaccumulative toxic (PBT) contaminant that poses a threat to the Great Lakes Basin environment. The text of our suggested comments follows.

The Vinyl Institute (VI), a business unit of The Society of the Plastics Industry, Inc. (SPI), supports the Environmental Protection Agency's (EPA) efforts to study and evaluate the effects of PBT's and other substances on the Great Lakes Basin. We understand that EPA has committed under the Great Lakes Binational Toxics Strategy to confirm that OCS is no longer used or released from sources that effect the Great Lakes Basin. While we recognize the origins of this task, we note at the outset the difficulty of proving a negative in an absolute sense. Thus, we assume that EPA's real task is to provide reasonable assurance that OCS is not intentionally used or released.

The draft OCS Report hypothesizes that OCS may arise from the production of ethylene dichloride (EDC), vinyl chloride monomer (VCM), and polyvinyl chloride (PVC) in three ways. First, the report identifies as "highly probable sources" of OCS the free radical pyrolysis of EDC to yield VCM, and the free radical initiated VCM polymerization process for the manufacture of PVC. Second, the report suggests that because OCS can be found in processes involving chlorine at high temperatures, the incineration of PVC can produce OCS. Finally, EPA asserts that whenever hexachl.orobenzene (HCB) is formed, the potential to form OCS exists.

The VI does not believe that the vinyl industry has any real impact on the Great Lakes Basin as it relates to OCS because:

- The EDC/VCM/PVC industry is located primarily outside the Great Lakes Basin;
- Existing control technologies would minimize any emissions of OCS that might be formed in the EDC/VCM manufacturing process;
- There is no reason to believe that any perchlorinated species can be created in VC polymerization;
- PVC disposal and incineration should not be a source of OCS; and
- Even a worst case analysis shows that the EDC/VCM/PVC industry would be a negligible source of OCS.

A. The EDC/VCM/PVC Industry is Located Primarily Outside the Great Lakes Basin

Members of VI are responsible for the majority of the domestic production volume of EDC, VCM, and PVC.[1] However, the vinyl industry has a limited presence in the Great Lakes Basin. All production of EDC and VCM in the U.S. occurs in Kentucky, Louisiana, and Texas. EPA itself acknowledges that there are no EDC/VCM production facilities in the Great Lakes Basin. Report at 53. In addition, more than 90 percent of U.S. PVC production occurs outside of the Great Lakes states. Indeed, the report only identifies a single location for PVC polymerization in the Great Lakes Basin. Report at 54.

EPA is also considering the potential for atmospheric deposition to be a source of OCS contamination in the Great Lakes Basin. However, EDC, VCM, and PVC production facilities are geographically located such that atmospheric deposition in the Great Lakes is so unlikely that it is reasonable to conclude that the industry is not a source of OCS in the Great Lakes region. This conclusion is supported by the history of OCS contamination in Lake Ontario sediments and in Lake Ontario trout. The report reflects decreasing OCS levels, approaching the near-zero level between 1921 and 1981. Report at 20. Similarly, concentrations of OCS in trout declined from 263 nanograms per gram in 1977 to 31.3 ng/g in 1993. During these periods of declining OCS releases to the environment, U.S. production of EDC, VCM, and PVC increased substantially to more than 25, 13, and 12 billion pounds a year, respectively. If the EDC/VCM/PVC industry was a source of OCS in the Great Lakes Basin, this would have been reflected in actual monitoring data.

B. Existing Control Technologies Would Minimize Any Emissions of OCS That Might Be Formed in the EDC/VCM Manufacturing Process

As acknowledged in the report, OCS is not deliberately manufactured, and the vinyl industry does not use OCS in any form. Further, based on knowledge and experience, any OCS that is unintentionally manufactured would be captured in the EDC or VCM purification process and/or emission control devices, which are strictly regulated under the Clean Air Act (CAA), Clean Water Act (CWA), and the Resource Conservation and Recovery Act (RCRA) to control emissions of hazardous air pollutants and other substances. As the OCS Report itself notes that "[t]here are no emissions released directly to the atmosphere [from EDC and VCM production facilities], as regulations require emission sources to be enclosed and all emissions to be collected." Report at 41 (emphasis added).

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[1]VI's members include: Borden Chemicals and Plastics Limited Partnership, CertainTeed Corporation, CONDEA-Vista Company, The Dow Chemical Company, Formosa Plastics U.S.A., The Geon Company, Georgia Gulf Corporation, Kaneka Delaware Corporation, Occidental Chemical Corporation, PPG Industries, Inc., Shintech, Inc., Union Carbide Chemicals and Plastics, and Westlake PVC Corporation.

As the report notes, gaseous streams are treated by incineration and liquid streams and wastewater are stripped of trace organics. In this regard, it is also important to note that incineration at EDC/VCM facilities, as well as PVC production facilities, is highly regulated and subject to continuous emissions monitoring. The incinerator operating parameters at these facilities provide a high degree of assurance. Further, the trace organics stripped from wastewater are typically routed back into the production process or to a well-controlled incinerator. Overall, OCS emissions are not a concern.

3 C. There Is No Reason to Believe That Any Perchlorinated Species Can Be Created in VC Polymerization

The VI has no data showing that OCS is formed during the polymerization of VCM. Although the report is not clear in this regard, it appears that EPA's speculation that PVC production is a source of OCS stems from an assumption that OCS is formed when polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F, or "dioxin") are formed, and that dioxin is formed during the polymerization of vinyl chloride. The VI does not believe that dioxin is formed during the polymerization process, and this conclusion is supported by the findings in the Vinyl Institute Dioxin Characterization Program Phase I Report (August 1998), which was previously submitted to EPA.

The OCS Report states that the formation of OCS in the PVC polymerization process "is not certain." From a chemistry perspective, we have no reason to believe that any perchlorinated species are created in the vinyl chloride polymerization process. Thus, the report's conclusion should be revised to state that OCS is not predicted to be formed during the polymerization process.

4 D. PVC Disposal and Incineration Should Not Be a Source of OCS

The OCS Report suggests that PVC products that are land-disposed rather than recycled or incinerated can be potential sources of OCS if accidental landfill fires occur. At the same time, the report indicates that all incineration processes involving chlorinated substances should be expected to form OCS. Studies on dioxin emission from commercial incineration systems indicate that the control of combustion conditions is the most effective way to minimize dioxin emissions.[2] It is reasonable to conclude that this technology would also be effective in the mitigation of OCS emissions. Further, modem landfill management practices mitigate the potential for landfill fires.

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[2] *See, e.g.,* "The Relationship Between Chlorine in Waste Streams and Dioxin Emissions From Waste Combustor Stacks," H. Gregor Rigo, *et al.,* American Society of Mechanical Engineers (1995).

E. Even a Worst Case Analysis Shows that the EDC/VCM/PVC Industry Would be a Negligible Source of OCS

Because the industry has little or no releases of OCS, the VI has not developed data on emissions of OCS from the vinyl manufacturing process. However, a worst case estimate can be constructed based on industry data and the OCS/dioxin ratio presented in the report. Please note that we have no basis to support the ratio factor of 653 for OCS to dioxin described in the report[3] Report at A-4. We use that figure here only to support the conclusion that the report should state that the vinyl industry is not a source of OCS.

If we assume that a relationship between the formation of dioxin and the formation of OCS in the EDC/VCM/PVC process exists, we can begin by basing an emissions estimate for OCS on dioxin emissions. In its August 1998, Dioxin Characterization Phase I Report, the vinyl industry indicated that the only potential release points of dioxin in the PVC manufacturing process were the incineration of the vinyl chloride recovery process vent, emissions from the polymer dryers, and wastewater. The recovery, process vent is regulated under the CAA's National Emission Standards for Hazardous Air Pollutant Emissions (NESHAP) to comply with a 10 parts per million (ppm) VCM emission limit in the vent stream.[4] For EDC/VCM production, dioxins were found in emissions from the process vent incinerators and wastewater, which are also regulated.

The report should note that the production of 12.5 billion pounds of PVC and 13.6 billion pounds of VCM from 25.5 billion pounds of EDC per year generates less than 31.3 grams on a Toxic Equivalent (TEQ) basis per year of dioxins to air and less than 0.22 grams TEQ/year of dioxins to water. As noted above, although we have no basis to support the ratio factor of 653 for OCS to dioxin that is described in the OCS Report, OCS emissions based on the suggested ratio of OCS concentrations to dioxin emissions can be estimated. Applying the ratio factor, total U.S. EDC/VCM/PVC production would emit less than 20.4 kilograms per year (kg/y) of OCS to the air and less than 0. 143 kg/y of OCS to water. In addition, these would be total national release numbers and would not reflect actual releases or deposition in the Great Lakes basin. The VI study found that over 98 percent of estimated dioxin releases originated from facilities that manufacture EDC/VCM or EDC/VCM/PVC, which, as noted above, are not located in the Great Lakes region. In sum, given EPA's estimate of 4,157 pounds (1,890 kg) per year emissions of OCS, the calculated worst case for the EDC/VCM/PVC industry contribution is so small as to be inconsequential.

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[3] The lack of an asserted correlation between a specific dioxin/furan congener and OCS adds further uncertainty to the OCS/dioxin ratio. This is particularly important since the small amounts of dioxin and furans produced in the EDC/VCM manufacturing process predominantly are the more highly chlorinated, less toxic species, such as octachlorodibenzo-p-dioxin.

[4] C.F.R. § 61.60 *et. seq.*

F. Conclusion

The Vinyl Institute does not believe that its industry has any real impact on the Great Lakes Basin as it relates to OCS because:

- The EDC/VCM/PVC industry is located primarily outside the Great Lakes Basin;
- Existing control technologies would minimize any emissions of OCS that might be formed in the EDC/VCM manufacturing process;
- There is no reason to believe that any perchlorinated species can be created in VC polymerization;
- PVC disposal and incineration should not be a source of OCS; and
- Even a worst case analysis shows that the EDC/VCM/PVC industry would be a negligible source of OCS.

The VI does not support the draft report's conclusions with regard to the vinyl industry and asks that they be revised to be consistent with these comments.